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*Preliminary Reports, Memoranda
and Technical Notes of the
Materials Research Council
Summer Conference*

La Jolla, California

July 1984

Sponsored by
Defense Advanced Research Projects Agency
DARPA Order No. 4000



Department of Materials and Metallurgical Engineering

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PRELIMINARY REPORTS, MEMORANDA AND TECHNICAL NOTES

of the

MATERIALS RESEARCH COUNCIL SUMMER CONFERENCE

La Jolla, California

July 1984

DARPA Order No.: 4000

Program Code No.: P4D10

Contractor: The Regents of The University of Michigan

Effective Date of Contract: 31 May 84

Amount of Contract: \$450,000

Contract No.: MDA903-84-K-0232

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Forward

This collection of papers does not constitute a formal reporting of the activities of the DARPA Materials Research Council Summer Conference. Each report, memoranda or technical note is a draft of the author or authors and is their work alone. The Steering Committee, in conjunction with the authors, will decide how this material can best be presented as a formal report to DARPA.

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WORKSHOP ON LOW DENSITY MATERIALS

A classified meeting was held on July 5-6 at the SAI facility in La Jolla on low density materials. The agenda and attendance lists are attached.

The meeting was arranged by S. G. Wax of DARPA and Professor J. L. Margrave of the MRC and Rice University at the request of the Lawrence Livermore National Laboratory.

The report of this meeting was transmitted to LLNL via DARPA and is not included in this report because of possible classification of some of the concepts.

AGENDA
LOW-DENSITY MATERIALS WORKSHOP

July 5-6, 1984

1200 Prospect Avenue
La Jolla, CA 92037

Thursday, July 5

Introductory Remarks	S. G. Wax, DARPA J. L. Margrave, MRC/Rice
Overview of Problem	LLNL Staff
Materials Needs	J. Robbins, LLNL Staff J. Richardson
Materials Development	A. T. Young, LANL Staff
Materials Development	J. G. Curro, Sandia
Foamed Graphites/Carbons	E. E. Hucke, U of M/MRC
Discussions of Doping Techniques	
(a) Printing technology for metals	W. Whitworth, Magnavox
(b) Fiber doping & processing	W. D. Timmons, Celanese
(c) Organometallic chemistry	J. L. Margrave, Rice/MRC
Discussion	

Friday, July 6

General Discussions

Chemical Doping Approaches

(a) Millefiore Glasses	Van Frechette, Alfred U.
(b) Organometallic Chemistry	M. S. Wrighton, MIT/MRC
(c) Polymer Blends	J. D. Hoffman, Maryland/MRC
(d) Metal Films	G. W. Kottang, 3M

Recommendations & Conclusions

MRC FOAMS WORKSHOP ATTENDEES

July 5-6, 1984

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BULK CRYSTAL GROWTH OF ELECTRONIC MATERIALS WORKSHOP

A. F. Witt and R. Mehrabian

INTRODUCTION AND OBJECTIVES

Traditionally the device matrix materials have been treated with benign neglect in device technology, primarily because the effects of matrix deficiencies on device performance and yield could not readily (if at all) be identified. This situation changed noticeably in silicon technology as (1) with increasing integration the linear dimensions of devices approached the effective dimensions of defects, and as (2) with increasing complexity of device processing the removal (deactivation) of process-induced impurities through internal gettering became mandatory. More recently, primary focus is placed on GaAs as substrate material for analog and digital IC fabrication, for power FET's, and for high power lasers. InP is attracting increased attention for integrated optics, very high speed lasers, LED's, and PIN detectors. CdTe-based ternary and quarternary systems continue to look attractive for IR focal plane arrays, electro-optic beam splitters and frequency doublers, tunable detectors, and for lasers in optical communications. Matrix deficiencies are recognized in all compound semiconductor systems and in some are found to control desirable advances in device technology. It should be noted that while the research volume on growth of semiconductors has increased in recent years, work on growth of oxides and oxide solid solutions has declined at an alarming rate during the same period.

While significant advances have been made in controlling and eliminating deficiencies in bulk electronic materials, the rate of advance appears to be exceeded by the rate at which property requirements become more stringent in advanced and projected device technology. Significant in

this context is the fact that growth technology is as yet based primarily on proprietary empiricism with a soft science base, and that technology transfer from R&D to production is painfully slow.

The primary objectives of this workshop were:

- (1) Assessment of the status of growth technology in the light of existing and projected needs of device technology.
- (2) Assessment of the status of the science base.
- (3) Identification of existing materials deficiencies, and their relationship to device performance and yield.
- (4) Identification of thrust areas to be pursued in melt growth of electronic materials.

The workshop comprised four invited presentations and a two hour discussion. Informal input was provided by members of the MRC and by invited guests. The agenda of the meeting and the list of attendees is attached to the end of this report.

SUMMARY OF PRESENTATIONS

Dr. L. Jastrzebski (RCA) focused on silicon substrate deficiencies and their effects on the development of circuits and device processing. He pointed out that the property specifications for Si wafers (beyond wafer size, flatness, and surface preparation) are not unique, but are a pronounced function of the device structure and even of adopted "fab line" procedures. Silicon may thus be classified (Table 1) into four categories with different processing temperatures, and related to these, with different sensitivity to defects. A comparative analysis of the status of silicon growth technology (Table 2) in broad terms appears to establish Japanese superiority. Recognized deficiencies in material produced by U.S. manufacturers relate to lack of reproducibility of growth deficient control of carbon incorporation, deficient control of precipitation kinetics, and residual

Table 1. Comparison of Different Processes

Process	Temperatures	Susceptability to Individual Defects	Design Rules	Wafer Diameter	Wafer Susceptibility to Warpage	Oxygen Concentration
Bipolar	few steps 1250°C	high; vertical short thru base; submicron defects	≈5 μm	3" and 4"	high	high 33-37 (ppm)
CMOS	1200-1150°C one step other lower	low	≈2-3 μm	4" and 5"	high-medium	medium 27-33 (ppm)
Dynamic NMOS	1050-1100°C or lower	high	≈1.5-2.5 μm	4" and 5"	low	very high (>37 ppm) high (33-37 ppm) medium (26-33 ppm) low (5-25 ppm) very low (<1 ppm) (FZ)
CCD imagers	1000°C	critically high	≈3 μm	3" and 4"	very low	low (5-25 ppm) very low (<1 ppm) (FZ)

Table 2. Status: Silicon Technology

COUNTRIES	DIAMETER CONTROL	RESIDUAL DOPANT LEVEL (ORDER OF)	CONTROL OF OXYGEN CONTENT	CONTROL OF CARBON CONTENT	CONTROL OF HETEROGENEOUS NUCLEATION
UNITED STATES	7"	10 ¹³	YES	NO/YES	NO
JAPAN	7"	10 ¹³	YES	YES	YES
WEST EUROPE	7"	10 ¹¹	YES	NO/YES	YES
EAST EUROPE	5"	10 ¹²	NO	NO	NO

impurity content. While the silane based Si-poly process developed by Union Carbide appears promising with regard to contamination control, no hard data are as yet available. Data are also unavailable on the property improvements achievable by magnetic field induced melt stabilization during growth.

There appears no difficulty in achieving increased crystal diameters. Crystals of 6 inch diameter are routinely grown; crystals with diameters of up to 12 inches have been grown in various laboratories. Implementation of processing technology for 6 inch diameter wafers is in process. The primary deficiencies in silicon growth technology relate to:

- (1) Control of the nucleation and growth of oxide precipitates.
- (2) Generation of non-equilibrium point defects during growth and dynamics of point defects following growth.
- (3) Defect formation during high temperature processing such as oxidation and epilayer formation.
- (4) Wafer warpage during device processing.

Approaches aimed at establishing the nature and origin of existing deficiencies, and at their elimination, are generally Edisonian, based on sophisticated empiricism. Emerging trends in silicon technology appear to focus on (a) control of oxygen precipitation, (b) development of immunity to latch-up and cross carrier injection, (c) increased device packing density, and (d) vertical device integration. Related materials problems have as yet not been identified.

In his summary, the speaker also remarked on the status of compound semiconductor device technology. He identified GaAs, InP, and CdTe as the technologically most important systems, and considered stoichiometry control, point and line defect formation, and twinning as the primary materials problems.

Dr. R. N. Thomas (Westinghouse) addressed the issue of melt growth of compound semiconductors for strategic defense applications, with primary focus on GaAs and CdTe.

Property requirements for GaAs based FET's and for both digital and analog IC's are only marginally met. The key issues continue to be excessive dislocation density, and type conversion of semi-insulating material. Approaches to overcome the formation of line defects focus on the use of iso-electronic doping with In at levels ranging from 10^{19} to $10^{20}/\text{cm}^3$ and on increasing the thickness of the B_2O_3 encapsulation layer. The respective effects of these approaches are commonly interpreted as solid solution hardening (increase in the critical resolved shear stress, CRSS) and a decrease in the axial and radial thermal gradients. Major complications arise also from turbulent melt convection, lack of stoichiometry control in LEC, and from crucible contamination. The semi-insulating nature of GaAs is attributed to compensation of silicon and carbon contamination by point-type defects which give rise to EL2 levels. The exact nature of the EL2 level is a subject of controversy. Application of magnetic fields for melt stabilization is anticipated to have major consequences on the density of EL2 states.

The first major program on LEC growth of CdTe has been initiated at Westinghouse. Preliminary experiments with 2 kg charges yielded "hollow" 2 inch diameter crystals which were polycrystalline. Complications of growth are attributed to the low thermal conductivity of both the molten and solid CdTe. Increased heat transfer from the crystal to the environment by increased forced convection in the ambient resulted in reduced "cavity" formations, but did not affect the degree of polycrystallinity. Addition of substantive amounts of ZnTe for the purpose of lattice hardening eliminated "polycrystalline" growth, but resulted in extensive laminar twinning parallel

to the growth interface. Twinning is as yet not under control, nor is the cause for twinning understood. A relationship between stacking fault energy (lowest for CdTe of all II-VI and III-VI compounds) and a tendency for twinning to occur; its exploitation for control of twinning is still pending. Application of magnetic fields to melt stabilization proved ineffective; this behavior is attributed to the lower electrical conductivity, and the high degree of molecular association of CdTe in the melt. Further advances in LEC growth of CdTe appear to be contingent on the development of means for improved heat transfer control.

Dr. A. Jordan (Bell Labs, AT&T) discussed "Bulk Growth of Compound Semiconductors: "Where Do We Stand, Where Are We Headed?" He identified major issues in III-V and II-VI materials used as substrates (Table 3) for device fabrication (Table 4). The primary issues, accordingly, are stoichiometry control, heat transfer control, and crucible contamination. The problems vary in degree from material to material and, moreover, are a function of device application and device processing procedures. A primary deficiency in all compound materials is the excessive formation of dislocations which appear to be related to the particular heat transfer characteristics of given growth systems. The factors influencing dislocation formation were identified (Table 5) as were their known adverse effects in device performance (Table 6). Guidelines for a comprehensive approach to growth of compounds with improved crystalline and chemical perfection were given: exploration of vertical growth systems with thermally quantifiable configurations (Kyropoulos technique, vertical Bridgman technique, and LEC with multiple heaters and diameter control); exploration of solid solution hardening effects by iso-electronic dopant; and determination of critical

Table 3. Some Major Substrate Issues

GaAs & InP	<ul style="list-style-type: none"> • Diameter control to obtain 2" or 3" round material
	<ul style="list-style-type: none"> - LEC: weight gain signal - HGF: shape conforms to vessel
GaAs	<ul style="list-style-type: none"> • Assurance of SI behavior and prevention of conversion
	<ul style="list-style-type: none"> - Use PBN crucibles - Avoid Cr - Undoped Si material by high pressure in-situ DS/LEC
InP	<ul style="list-style-type: none"> • Understanding of reproducible Si behavior in Fe-doped crystals
InP & CdTe	<ul style="list-style-type: none"> • Elimination of twinning and multiple nucleation
GaAs, InP & CdTe	<ul style="list-style-type: none"> • Dislocation genesis and reduction

Table 4. Some Device applications of Compound Materials

GaAs (SI)	Microwave low noise and power FETS Analog and digital ICs SDHTs
GaAs (n-type)	0.87 μm high power lasers for writing and reading LEDs
InP (SI)	Integrated optics Very high speed laser
InP (n-type)	1.3 μm zero dispersion multimode lasers 1.55 μm minimum loss single mode lasers 1.3 μm LEDs 1 - 1.7 μm APD and p-i-n detectors
CdTe	Electrooptic beam splitters and frequency doublers 3 - 40 μm $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ lasers for optical communications at $\sim 4\mu$

Table 5. Some Factors Influencing Dislocation Formation

Ambient temperature:	A low ambient temperature gradient suppresses dislocation generation.
Radius	The dependence of dislocation density on r_0 turns sublinear at larger r_0 .
CRSS:	A large value inhibits dislocation formation. Impurity hardening by: isoelectronic impurities: GaAs(In) n-type dopants: GaAs(Si or Te) InP(S, Sn or Ge)
Heat transfer coefficient:	The prevailing large h is adverse to dislocation density reduction.
Time:	Maximum in σ_{ex} at the top of the crystal as a critical time is reached.
Pull rate:	A slow p provides a minor benefit in lowering the dislocation content.

Table 6. Adverse Effects Attributed to Dislocations

- Minority Carrier Devices
 - Accelerated degradation rate of GaAs LEDs
 - Reduced quantum efficiency of Si-doped GaAlAs LEDs
 - DLDs in GaAlAs lasers
 - Microplasmas in InP-based APDs
- Majority Carrier Devices
 - Large swings in the threshold voltage of GaAs FET arrays
 - Variation in the drain-source current of GaAs FETs
 - Sheet resistance, leakage current and EL2 level track the dislocation distribution in SI GaAs

resolved shear stresses as a function of dopant concentration and temperature. In connection with growth experiments, a multi-pronged approach to characterization is to be developed: dislocation density, resistivity, mobility, EL2 level, IR absorption, etc., are to be recorded with their x-y coordinates on given wafers; the data are to be sorted, and cross correlations on a micro- and macroscale are to be determined by computer. As indicated, the characterization is to be repeated after wafer processing, such as ion implantation, and significant property changes are to be identified. The data obtained are to be used for the identification of correlations between device yield, device performance, and substrate properties. To achieve improved bulk materials, it appears mandatory that the science base for industrial melt growth be strengthened. Meaningful theoretical approaches to heat transfer and the fluid-dynamics of melts are essential. The usefulness of modelling, however, is ultimately controlled by the availability of thermo-physical data for the systems of concern. These data (thermal conductivity of liquids and solids, expansion coefficients, elastic constants, emittance, CRSS, and melt viscosities are as yet unavailable. It is speculated that meaningful progress will be made as these data become available. Recommendations are summarized in Table 7.

Dr. C. D. Brandle (Bell Labs, AT&T) presented a status report on melt growth of oxides for device application. The development of new oxide materials and research on growth of conventional and new materials has declined over the past fifteen years at an alarming rate (Table 8). Comprehensive research capabilities have been virtually decimated in the West, while Eastern European countries continue, at the same or an increased level, exploration of new oxide materials systems. The decline in oxide growth is in part attributed to high cost of raw materials and crucibles.

Table 7. Recommendations for a comprehensive approach to bulk melt growth of compound semiconductor materials.

- Optimize temperature gradient and hardening agent additions in the LEC growth of GaAs and InP.
- Improve thermal geometry of LEC systems by means of reflectors and additional heaters.
- Explore novel horizontal and vertical configurations (Computerized Dynamic Gradient, LEK).
- Ascertain benefit of MLEC.
- Reduce incidence of twinning in CdTe by adding Mn.
- Advanced numerical modeling including synthesis of fluid flow and heat transfer analyses.
- Measure high temperature physical properties required in computer simulations.

Table 8. Trends in Crystal Growth

	Oxides	III-V	II-VI	Halides	HYDO & C
1966	63	15		14	8
1968	47	18	15	12	8
1971	41	31	9	8	11
1974	41	37	7	12	3
1977	40	30	5	5	20
1980	47	24	6	9	14
1983	20	43	18	6	13

inadequate purity of starting materials, complexity of mixed oxide systems, and in part to the emergence of substitute organic polymers. It was pointed out that the potential of oxide materials has not as yet been realized, primarily because the earlier focus was placed on production and because meaningful research was impeded by the unavailability of pure systems and of adequate growth facilities.

The primary deficiencies in growth of oxides are analog to those in compound semiconductor systems, namely: composition control (Table 9), control of fluid dynamics in the melt (Table 10), and diameter control Table 11). The specific problems associated with growth of oxide solid solutions (Table 12) are second phase formation, dopant uniformity, compositional gradients, interface breakdown, and lattice strain -- also encountered in binary and pseudo-binary semiconductor systems with large liquidus-solidus separation.

If oxide systems are to reach their true potential, meaningful research must revert to the classical tungsten-bronze systems, making use of purified charges and of information gained on effective heat and mass transfer control.

It is essential that relevant properties of organic polymers and their processing into devices be explored before the level of research activities on growth of oxides is further reduced. (Relevant electro-optical constants are given in Table 13.)

PERSPECTIVES AND ISSUES

Evidence provided during the workshop strongly suggests that the U.S. is losing its leadership in the production of high quality bulk grown crystals to Japan. If this trend continues, it is conceivable that the U.S. solid state

Table 9. Composition Control Requirements

- Most complex oxides are not stoichiometric
- Must grow at the congruent composition
- Detailed knowledge of the phase diagram in the region of interest absolutely necessary
- Atmosphere composition, i.e., O_2 partial pressure does effect solid composition

Table 10. Fluid Dynamics

Determined by:

- Liquid Thermal Geometry
- Crystal Rotation & Growth Rate
- Crucible Geometry
- Furnace Geometry

Influences:

- Interface Shape
- Dislocation Structure
- Dopant Distribution
- Strain Distribution
- Growth Striations

Table 11. Diameter Control Weight Method

Assumptions:

- No buoyancy effects
- Constant shape growth interface
- Uniform cross section throughout the crystal length

Advantages:

- Control equipment and techniques well developed
- No visual information required
- No size restrictions on crystal

Disadvantages:

- Crystal cross sections do change
- Interface shape can change during growth
- Does not work for $k > 1$ materials

Table 12. Solid Solutions

Uses:

- Lasers (Nd:YAG)
- Electro-Optic ($\text{Ba}_{1-x}\text{Sr}_x\text{Nb}_2\text{O}_6$)
- "Stoichiometric" (LiNbO_3)

Problems:

- Second Phase Formation
- Dopant Uniformity
- Compositional Gradients
- Interface Breakdown
- Strain

Table 13. Electrooptic Constants for Crystals

1) Oxides:

MATERIAL	γ_{33}	γ_{13}	γ_{42}	FIGURE OF MERIT F	TEMPERATURE
(UNITS OF 10^{-12} M/V)					
BaTiO_3	---	---	3,000	$24,000 \cdot 10^{-12}$ m/v	0°C
			1,700	$13,600 \cdot 10^{-12}$ m/v	20°C
$\text{Sb}_{0.75}\text{Ba}_{0.25}\text{Nb}_2\text{O}_6$	1,300	66	42	$7,800 \cdot 10^{-12}$ m/v	20°C
$\text{Pb}_{0.6}\text{Ba}_{0.4}\text{Nb}_2\text{O}_6$	---	---	1,300	$7,800 \cdot 10^{-12}$ m/v	20°C
$\text{K}(\text{Nb}_{0.5}\text{Ta}_{0.5})\text{O}_3$	400	---	---	$2,400 \cdot 10^{-12}$ m/v	20°C
K NbO_3	300	---	---	$1,800 \cdot 10^{-12}$ m/v	20°C

2) Polymers:

	γ_{11}	γ_{42}		
PVF_2		0.21		20°C
2 methyl + nitroaniline	67.		$270 \cdot 10^{-12}$ m/v	20°C

device technology will become dependent on foreign sources for bulk single crystals. Available research support comes primarily from DoD (DARPA); the total research effort, enjoying only token corporate support, is subcritical and inadequate to meet existing needs. Although U.S. research on growth of compound semiconductors has increased during the past several years, concurrent advances in device technology render substrate properties more critical today, and residual deficiencies in bulk material emerge in several device areas as yield and performance controlling. The research level on growth of elemental and compound semiconductors in the U.S. lags significantly behind that of Japan, and likely also behind that of Western Europe. As commented by several attendees of the workshop, our research effort lacks focus and coordination; in many instances research is carried out at a subcritical level; above all, there is evidence that science and technology transfer from R&D to production is excessively slow. Conspicuous for many systems is the lack of correlations between wafer behavior during device processing and identified deficiencies in bulk materials. Also conspicuous is the apparent lack in reproducibility of melt growth.

The community was unanimous in its belief that progress in industrial crystal growth is contingent on the reinforcement of the science base of this traditionally empirical activity. Meaningful modelling of heat, fluid and mass transport phenomena during growth are key elements to desired advances. Such modelling is currently impeded by the virtual unavailability of thermo-physical data. It was also stated that modelling must be carried out iteratively with parallel experimental work.

Available evidence indicates that solutions to existing growth problems will require involvement of complementary expertise in the areas of transport phenomena and solidification, diagnostics and sensors control

theory , and the use of physical metallurgists versed in mechanisms responsible for strength and structure.

RECOMMENDATION

A. General Recommendations

1. Improvement of Bulk Crystal Growth.

There is a strong need to develop controlled bulk crystal growth techniques based on improved process models, new sensors (in-situ variety), and understanding of relationships between growth environment and conditions and degree of purity and perfection. This can be accomplished through a coordinated program that integrates "experts" from various specialties, including electronics, metals, process modelling, controls, etc.

2. Establishment of a reliable thermo-physical data base for industrially relevant materials (Si, GaAs, etc.).

The availability of thermo-physical data is the basis for the conversion of crystal growth from a state of proprietary empiricism to a science based activity. Focus should be on the use of these data to study the thermodynamics and kinetics of liquid to solid transformation, solute segregation, heat and fluid flow and mass transfer.

3. Process Models

Two- and three-dimensional models of real geometrics are needed. Coupling of these models to experiments is essential for optimized crystal growth under real-time control. Fundamental understanding of the turbulent-like flows in

large-scale Czochralski growth systems is needed before interaction of these flows with magnetic yields can be predicted.

4. New Techniques

Exploration of the capabilities of non-conventional growth systems such as magnetic Czochralski pulling and vertical Bridgman growth should be pursued.

5. A number of important phenomena that affect the strength and structure of semiconducting crystals are not well understood. These include the formation and multiplication of dislocations, interaction of stacking faults with solute atoms, solid solution hardening by isoelectronic alloying elements, mechanism of twinning and the formation, structure and distribution of precipitates. A strong science base in physical metallurgy exists in this broad field. The expertise available should be integrated into future investigations (see J. C. Williams and J. P. Hirth write-up).

B. Recommendations Concerning Specific Materials Systems:

Silicon: While growth of device quality silicon is considered a non-issue, it is well-established that even the best available material is deficient for both intrinsic and extrinsic IR detectors and inadequate for large area focal plane arrays. Moreover, device yield in VLSI technology fails to even approach theoretical limits. Issues of concern that should be pursued are:

- a. Incorporation of oxygen and heterogeneous nucleation of oxide precipitates; the structure, composition and state of coherency of these precipitates needs to be characterized.

- b. Non-equilibrium point defect generation and dynamics of these point defects after growth;
- c. Radial uniformity of dopant incorporation;
- d. Solid solution hardening effects of dopants in crystals of large diameter;
- e. Growth of silicon by the float-zoning techniques. While oxygen/internal gettering at this time precludes the use of float-zoning, there is no assurance that external gettering procedures (or oxygen doping in FZ-silicon) will not emerge; this country is presently devoid of FZ technology and thus is in some sense vulnerable.

Gallium-Arsenide: The growth process of this material is in essence as yet uncontrollable, i.e., non-reproducible. Issues of concern are semi-insulating properties without type conversion, suppression of thermal stress induced dislocations, spatially uniform iso-electronic doping, incorporation of dissolved gases, residual contamination of the charge constituents and contamination of charges by crucibles, thermo-physical properties of B_2O_3 (encapsulant) and their change during growth, and diameter control.

Research focus should be placed on:

- a. Heat transfer modelling and control aimed at minimizing axial and radial thermal gradients in growing crystals;
- b. Establishment of optimized thermal melt stabilization through applied magnetic fields;
- c. Solid solution hardening by means of iso-electronic doping, and a better understanding of hardening mechanisms including possible hardening by interstitial atoms.

- d. Stoichiometry control of encapsulated melts during growth;
- e. Determination of the nature (composition and structure) and origin of EL2 levels and their formation during growth;
- f. Determination of the effects of low and high pressure GaAs synthesis on melt properties and on defect formation during LEC growth of GaAs;
- g. Optimization and on-line control of growth conditions based on modelling of heat and fluid flow and mass transfer phenomena in real growth systems.
- h. Development of a comprehensive approach to characterization aimed at the establishment of correlations between device yield/performance and bulk matrix deficiencies.

Indium Phosphide: All issues of concern for growth of GaAs are relevant also for growth of InP. In addition, a comprehensive effort should be made to determine the origin of twinning.

Cadmium Telluride: All issues of concern for growth of GaAs are also relevant for growth of CdTe. Identification of the mechanism of twinning is needed in order to select minor solute additives to inhibit their growth. Primary focus should be placed on means for overcoming the adverse effects of low thermal conductivity in both the liquid and solid state.

Growth of Oxides: Considering the fact that melt growth of oxides has not as yet matured and that the production of organic polymers and their anticipated partial replacement is as yet in preliminary R&D stages, the experienced decline in related research activities must be considered as alarming. It is recommended that DARPA maintain a critical support level

for research on growth of oxide systems for opto-electronic device application. Research could focus on:

- a. Melt composition -- congruency, stoichiometry, impurities;
- b. Atmospheric conditions -- effects of composition and pressure of ambient on the defect structure in the grown material;
- c. Heat flow and solidification -- heat transfer, growth interface morphology, non-equilibrium segregation effects, lattice strain.

Specifically, it is suggested to pursue:

1. A rational design of new oxide materials for:
Electro-optics: Integrated optics
Spatial light modulators
Photo-refractive holography
Piezoelectrics: SAW: H.F. transduction
Dielectrics: High K, flat T_c
Pyroelectrics: High $\partial P/\partial T$, low K
2. The design of better techniques for growing oxide solid solutions -- off congruency.
3. The establishment of more reliable phase diagrams for current growth methods.
4. New morphotropic phase boundary compositions to exploit phase transition enhancement of bulk properties (d_{15} , χ_{42} , etc.).
5. The design of techniques for growth of highly grain-oriented micro-polycrystals.

AGENDA
CRYSTAL GROWTH: BULK AND EPITAXIAL

Materials Research Council
Torrey Pines Elementary School
La Jolla, California

July 9-10, 1984

MONDAY, July 9

Introductory Remarks - G. Vineyard

Session I. Bulk Crystal Growth, Chairman, A. Witt

Material Deficiencies and their Effects on the Development of
Circuits and Device Processing.
L. Jastrzebski, RCA Labs.

Melt Growth of Elemental and Compound Semiconductors for
Strategic Defense Applications.
R. N. Thomas, Westinghouse R&D Center

Melt Growth of Oxides for Device Application: Status and
Projection, C. D. Brandle, AT&T Labs.

Bulk Growth of Compound Semiconductors: Where Do We Stand?
Where are we headed? A. Jordan, AT&T Labs.

Session II. Epitaxial Growth, Chairman, T. C. McGill

Molecular Beam Epitaxy for III-V Semiconductors,
A. R. Calawa, Lincoln Labs.

Molecular Beam Epitaxy of II-VI Semiconductors,
J. P. Faurie, Univ. Illinois

MOCVD Deposition of Semiconductors,
R. S. Burnham, Xerox, Palo Alto Res. Ctr.

TUESDAY, July 10

Session III. Theory of Crystal Growth, Chairman,
R. Mehrabian

Thermodynamics of Interfaces and Crystal Growth,
J. Cahn, NBS

Growth Interface Kinetics and Stability , R. Sekerka
Carnegie-Mellon Univ.

The Role of Modeling in the Optimization of Semiconductor
Crystal Growth, R. A. Brown, M.I.T.

Session IV. Chairmen, H. Enrenreich and J. Hirth

Discussion

ATTENDEES

CRYSTAL GROWTH: BULK AND EPITAXIAL July 9-10, 1984

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STRENGTHENING AND STRUCTURE OF SEMICONDUCTING CRYSTALS

J. C. Williams and J. P. Hirth

There are several issues which were discussed during the crystal growth sessions that merit reconsideration using the background information from physical metallurgy and materials science. These are:

- solid solution hardening
- solute-stacking fault interactions
- growth twin formation
- precipitation
- formation and multiplication of dislocations.

The purpose of this discussion is to summarize these points and to suggest some experiments that may be useful.

SOLID SOLUTION HARDENING

Solid solution hardening of metallic alloys has been used extensively. In semiconductors the introduction of isoelectronic alloying elements is being considered to increase the resistance to dislocation formation and multiplication. It may be useful to recall the ways in which solute atoms and dislocations interact in order to think about the role of isoelectronic alloying additions. These are elastic, modulus, stacking fault, electrical, chemical (local order), and Peierls stress (local bonding) interactions. Of these the most significant for isoelectronic solutes are probably elastic and Peierls stress although little is known about modulus or stacking fault interactions. It has been suggested that isoelectronic solutes retain their original bond lengths when in solid solution. If this is the case then the local misfit can be large and the elastic and Peierls interaction with dislocations

can be strong. Moreover if the misfit is anisotropic due to this bond length effect, then local reorientation in the stress field of edge dislocations may also occur (the Snoeck effect) which will further strengthen the interaction.

Additionally, coupled measurements of atomic bond lengths (EXAFS) and long range strain (x-ray diffraction) are needed for a variety of isoelectric solutes. Once these misfit parameters are known, the hardening due to different isoelectronic solutes can be more readily understood. It is also important to determine the concentration dependence of the hardening. In addition to isoelectronic solutes, other solute interactions in electronic materials would be important from a hardening viewpoint. This is especially true for elements which may dissolve as interstitials (e.g., O in Si) because interstitials produce more rapid hardening.

STACKING FAULTS

Stacking fault interactions may also be important both in Si and in CdTe, but possibly for different reasons. There often is a thermodynamic reason for solutes (impurities) to segregate to stacking faults. If this occurs the fault is pinned and the flow stress increases (Suzuki hardening). If solute segregates to the fault, it generally extends so that a given density of dislocations results in a larger stacking fault area per unit volume. This has implications with respect to electrical properties, so that strengthening due to stacking fault pinning may not be desirable. With electronically active dislocations in II-IV compounds, another possibility may be that charge effects dominate, influencing both stacking fault energy and dislocation extension in either direction.

TWINS

In CdTe the stacking fault energy is low enough to lead to a high frequency of growth twins. These twins are undesirable and there has been discussion of alloying with isoelectronic elements (e.g., Mn) to increase the fault energy and reduce the incidence of twins. It is generally true in metallic alloys that solute additions lower rather than raise the stacking fault energy, thus, it is suggested that judicious selection of solutes based on sound physical reasoning will be essential to achieving an increase in stacking fault energy if this is possible at all. A more attractive approach may be to identify the mechanism of twinning (e.g., pole mechanism) and then add minor solutes to inhibit the action of this mechanism (e.g., pinning the mobile partial dislocation that revolves around the pole).

PRECIPITATION

There also is a great deal of interest in the formation of precipitates in Si and GaAs. The nature of these precipitates, such as their structure, composition and state of coherency, does not seem to be well-characterized. However, the formation of second phases by nucleation and growth in metal and ceramic matrix materials has been studied extensively. It is known that the distribution of precipitates and the kinetics of their formation sensitively depend on the details of the system. Thus, without a priori knowledge of the precipitation process it is not possible to predict the spatial distribution of precipitates or the kinetics of their formation. Moreover, in some instances (e.g., hydride formation in Ti, Zr or Hf) the role of solid solution strengthening solutes can interact with the precipitation process not only by altering the thermodynamic driving force,

but also by increasing the stresses required for plastic accommodation of the precipitate volume change in the matrix. In such cases metastable solubility can increase significantly and the kinetics of precipitation can be slower or precipitation can be completely suppressed. In view of this, the precipitation of impurities in semiconducting crystals can be delayed, a process which can be troublesome if precipitation at gettering sites is a desirable event. Also, when precipitation occurs, there may be an accompanying increase in dislocation density around the precipitates due to plastic accommodation. Alternatively, if the impurity content is assumed to be soluble, but is actually in metastable solid solution, then the introduction of damage (e.g., by handling) can lead to heterogeneous nucleation of precipitates and a rapid change of impurity concentration in solution.

DISLOCATIONS

Finally, there is interest in the mechanism of dislocation generation during crystal growth and processing. There have been some calculations performed which permit an estimate of the thermal stress. There also have been some elevated temperature flow stress measurements on as-grown crystals. There appears to be a temptation to compare this flow stress and the thermal stress to decide if dislocations can be generated by thermal gradients. Unfortunately, such comparisons beg the question of the theoretical shear stress required to initially introduce dislocations. The thermal stress may support the multiplication of existing dislocations but they do not appear to be high enough to account for the initial dislocation formation, at least given the data that currently exists. In this regard the nature of the grown-in dislocations and measurements of the flow stress as

a function of temperature, particularly at temperatures very near the melting temperature (or solidus temperature) may prove instructive. Some dislocation punching experiments, which would provide a measure of the local stress required to inject dislocations into the lattice, would also be useful. Under varying growth rates, both solute segregation via cellular growth and generation of vacancy supersaturation can occur, both processes which favor the generation of dislocations during the crystal growth process.

Finally, the redistribution of solute during crystal growth, both edge to center and end to end, potentially is very important to the strength and structure. Here also, there is considerable work which can be brought to bear on this subject but does not appear to have been considered in detail. Local variations in composition can lead not only to local variations in electrical properties but also to local variations in strength and in propensity for dislocation generation and precipitate formation. This should be considered as part of the overall picture of strength and structure of semiconducting crystals.

FORMATION OF NEW PHASES FROM SYSTEMS THAT ARE NOT IN METASTABLE EQUILIBRIUM

J. Cahn

Classical nucleation theory assumes that the system has reached a state of full metastable equilibrium. Not only is the free energy stationary with respect to all infinitesimal changes but all small enough finite changes raise the free energy. Nucleation theory concerns itself with finding the path with the smallest free energy increases that leads to phases with negative free energies of formation. This restriction on requiring the initial state to be metastable is an important simplification that is valid for many but not all cases of interest. It originated with Gibbs, whose analysis proceeded according to the scheme, simplified for isothermal constant pressure transition, is depicted in the flow chart of Fig. 1. For nonisothermal systems and ones that interact with various devices capable of doing work, the criterion becomes the entropy changes and constant global energy but the scheme remains the same.

Not all formation of new phases occurs by nucleation. Second-order transitions and spinodal decomposition are examples of continuous phase change without a free energy barrier that can occur from systems that are thermodynamically either unstable or in unstable equilibrium. Phase transition sequences have been observed in which the system evolves through several phase transitions without ever reaching metastable equilibrium.

Unless special care is taken, few systems ever reach full metastable equilibrium before new phases appear. The question is: When are predictions of nucleation theory seriously affected by the absence of the two conditions for inelastability? The answer seems to depend on whether or not

the dissipative processes occurring in the system couple into the phase change mechanism.

Examples of cases where new phase formation occurs in systems that are not in metastable equilibrium abound. It is convenient to consider two types of systems, those that are isolated except for thermal reservoirs and a constant pressure environment, and those subject to continuous addition of energy.

Continuous irradiation and plastic deformation are two examples of the latter. Because free energy is continuously dissipating, localized free energy changes just due to phase changes are no longer a valid criterion. Indeed irradiation is known to alter the stability of phases. Phases stable in the absence of irradiation are known to disappear and phases not stable in the absence of irradiation can appear. An entirely different nucleation theory has been developed for irradiation. (K. C. Russell). In the theory the annihilation of point defects occurs on the interphase interfaces. Vacancy condensation removes atoms and causes the new phase to shrink, while interstitials cause it to grow. The stress field around the phase biases the defect fluxes. This is an example of coupling of damage annealing to phase change, which hardly affects the free energy of phases, yet can cause drastic changes in their stability.

Initially unstable systems that have no continuing input of energy evolve. If they land in inelastable wells, nucleation theory becomes applicable. If the dissipative processes occurring before inelastable equilibrium is reached couple into the phase change process, transient effects on the nucleation of the type discussed above could be very significant. A simpler transient effect could be that the driving force

changes with time as the system evolves, or that a surface on which heterogeneous nucleation could occur is changing.

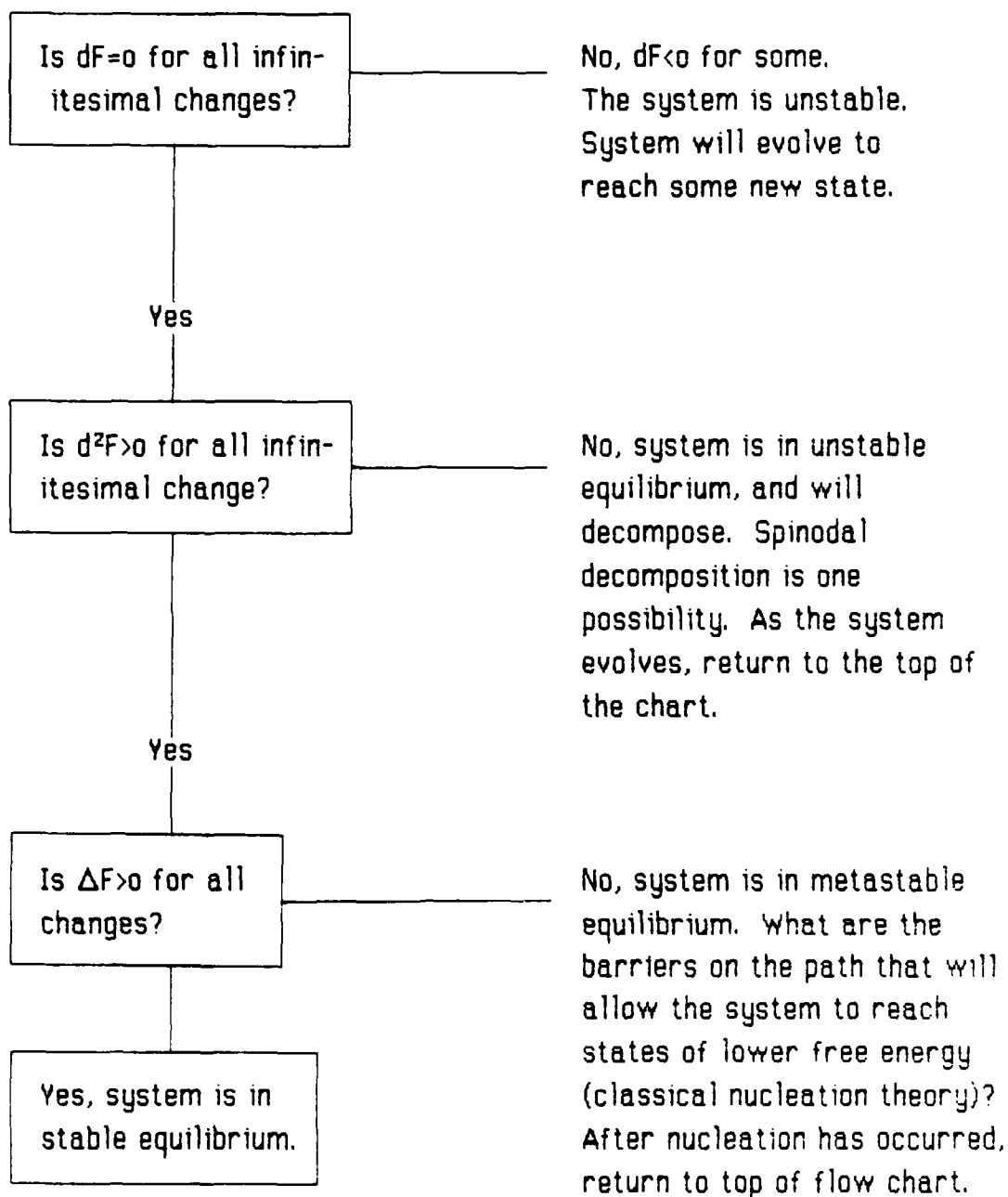
It is entirely possible that an unstable system never lands in metastable wells and yet evolves to quite different new phases through first order transitions without any thermodynamic barriers. For example, fcc iron can precipitate from copper by a spinodal mechanism at a temperature where bulk fcc iron is unstable, coarsen to a size where spontaneous coherency loss is followed by a martensitic shear to form bcc iron. Many complex phase sequences occur without the system ever reaching a metastable well. Within classical nucleation theory there are limits where barriers disappear. Nucleation on a surface that is perfectly wet by the new phase is one such example. Nucleation of an incoherent phase on a dislocation is a case where a metastable state can be reached at low driving forces, but this metastable state disappears at high driving forces, and the new phase can grow continuously. New phase formation along non-equilibrium interfaces such as Al/GaAs is possibly a case where no metastable state is ever reached.

Nucleation theory often predicts that single atoms are nuclei at high supersaturation. Clearly this is barrierless nucleation and new phase formation is better described by coarsening theory.

Most present theories of the kinetics of phase changes from unstable systems are based on kinetic master equations. Diffusion in real space as in spinodal decomposition, or in size space as in Russell's radiation damage theories, and in the older coarsening theories are example of such equations that attempt to predict how the system evolves. No general master equations have been developed. The solution to these master equations

sometimes reveal phenomena that mimic nucleation and in certain limits reduce to nucleation theory. The Lyapunov function used for testing mathematical stability of solutions often is the free energy, but there are many cases, e.g., phase evolution during irradiation where it is not. There are many cases where these equations show how new phases form in continuous way that in no way resemble nucleation theory.

FIGURE 1



A MECHANISM FOR THE REDUCTION IN DISLOCATION DENSITY IN AS-GROWN GaAs CRYSTALS BY INDIUM ADDITIONS

J. P. Hirth and H. Ehrenreich

Introduction

At the MRC meeting on Crystal Growth, R. N. Thomas presented data indicating that the addition of a few percent In to GaAs by growth from the melt greatly reduced the dislocation density. After growth, the dislocation density at the center of the crystal was decreased several orders of magnitude to $\leq 10^2/\text{cm}^2$. In the discussion, this problem was identified as one requiring a theoretical rationalization to provide guidelines for similar effects in other systems. In the present work, we show that the effect can be explained in terms of solid solution hardening. The entities providing the hardening, unlike typical metals where a single solute atom suffices, are 5 atom clusters bounded by anions.

Defect Model

Mikkelsen and Boyce¹ have studied bond lengths by EXAFS in the (Ga, In) As system. They find that the bond length of the Ga-In sublattice, and correspondingly the lattice parameter, follow a mean field approximation with both quantities increasing linearly with In concentration. The As sublattice, however, does not follow such a variation. Instead the Ga-As and In-As bond lengths vary little with In concentration, remaining roughly constant as x is varied in $\text{Ga}_{1-x}\text{In}_x\text{As}$. Second-neighbor bond lengths, together with the other result, suggest that the four As neighbors of Ga or In retain roughly a tetrahedral configuration but collapse around Ga and expand around In. Support for such a model is provided by the work of Hass et al² who performed molecular coherent potential calculations in a

tight-binding model. They showed that scattering including both structural and chemical effects could be modelled in terms of such regular arrays of 5 atoms, with substantial contributions from the structural bond-length changes but with the chemical effect being dominant (~60% of the band shift). Consistently, the relatively weak bond-length change with x varying from 0 to 1 (1% compared to a lattice parameter change of 7 percent) implies that chemical bonding is dominant over lattice strain in determining the structure of the ternary crystals.

With even greater strain contributions, as in CdGeAs_2 where the lattice parameter varies by 11 percent, the strain is sufficient to produce the strain-induced ordered structure of chalcopyrite³. For $(\text{Ga},\text{In})\text{As}$, however, there are no indications of ordering of In and Ga, the maximum degree of order for the most favorable $x=0.5$ composition being 10 percent within experimental error¹.

In view of these findings, the $(\text{Ga},\text{In})\text{As}$ solution is treated in terms of In solute defects in a GaAs matrix. The defects comprise uniformly expanded InAs_4 tetrahedral units with a bond extension of 7 percent, equal to the change in lattice parameter or bond-length in going from pure GaAs to pure InAs. The resultant elastic strain field can be represented by four tensile point forces with tetrahedral symmetry acting at a point. The long-range field of such a point-force distribution is equivalent to the extension of a spherical hole of radius $r_0 = 0.2450 \mu\text{m}$ (the original Ga-As bond length) by a volume dilatation of 21 percent⁴.

Dislocation Interaction

The above size misfit of 21 percent is relatively large compared to typical metal systems, so an appreciable solid solution hardening effect is to be

expected. The elastic interaction energy between a misfitting sphere and an edge dislocation is⁵:

$$W = \mu(1+\nu)\delta v \cdot b \sin \Theta / 3\pi(1-\nu)r = B b \sin \Theta / r \quad (1)$$

with μ = the shear modulus, ν = Poisson's ratio, $b = 0.4001 \mu\text{m}$ is the magnitude of the Burgers vector, and r and Θ cylindrical coordinates with z parallel to the dislocation line. The volume change δv is related to the above-mentioned dilatation of:

$$\delta v = eV = 0.21v = 0.21(4/3)\pi r_0^3 \quad (2)$$

The elastic constants⁶ $c_{11} = 11.9 \text{ GPa}$, $c_{12} = 5.99 \text{ GPa}$, $c_{44} = 5.38 \text{ GPa}$, and $H = 2c_{44} + c_{12} = 4.85 \text{ GPa}$ for GaAs are assumed to apply as well for the dilute In solution. Isotropic elasticity is also assumed with the Voight average values:

$$\mu = c_{44} - 0.2H = 4.41 \text{ GPa} \quad (3)$$

$$\nu = (c_{12} - H/5) / 2(c_{44} + c_{12} - 2H/5) = 0.27$$

Substitution into Eq. (1) gives $\beta = 0.067 \text{ eV}$. The maximum interaction force at $\Theta = \pi/2$ is given by⁷:

$$F \equiv W(r=b)/b = \beta/b \quad (4)$$

This is also the pinning force that must be overcome by the applied stress to move a dislocation. The appropriate geometry is shown in Fig. 1.

The pinning force is balanced by the projected components of the dislocation line tension, $T=1/2 \mu b^2$ in a simple line-tension model. Thus, for the critical bowout angle ϕ_c ,

$$F = \beta/b = 2T \cos \phi_c/2 \quad (5)$$

The line tension force in turn balances the force from the applied stress, resolved on the glide plane, σ .

$$F = \sigma bL \quad (6)$$

From the above value for β we calculate $(\phi_c/2) = 87.9$ degrees. For a composition $x = 0.03$, the glide plane spacing between solute In atoms is $L = 4b$. Then, equating relations (5) and (6), we calculate a breakaway stress:

$$\sigma_c = 0.01\mu = 41 \text{ Mpa.} \quad (7)$$

This value of σ_c corresponds to the predicted resolved flow stress influenced by solid solution hardening in an In alloy with $x = 0.03$.

Implications for the Strength of GaAs

A comparison with Eq. (7) shows that the solid solution hardening increment is substantial. A remaining problem is the temperature dependence of the flow stress for the solution hardening case. Of course, for GaAs, brittle fracture intervenes for temperatures below about 300°C. A representative curve for a metal solid solution hardening system is shown in Fig. 2, with T_1 generally below room temperature and T_2 at about 0.6 to 0.7 T_m , the melting point. Dislocation models of flow could suggest

qualitatively similar behavior for compound semiconductor crystals, but the ratio of T_2/T_m might vary with crystal system.

Thus, the results clearly indicate that In should provide strong solid solution hardening of GaAs at room temperature, and incremental hardening at elevated temperature. The hardening could plausibly explain the decrease in dislocation density in GaAs alloys grown with 2-3 percent In additions. Studies of the temperature-dependent flow stress and/or hardness of (Ga, In) As alloys would be helpful in clarifying the situation at elevated temperature.

Implications for Other Properties of GaAs

The finding that chemical bonding dominates over strain energy in establishing the configuration of In in solution in GaAs has other implications. In strained superlattices, consisting of 8 to 20 μm thick alternating layers of semiconductor compounds, the simple view is that the interfaces between layers are sharp, coherent and free of misfit dislocations. As a consequence there is an abrupt change in elastic strain at the interface from $\sim +\epsilon$ to $\sim -\epsilon$ with ϵ ranging up to ~ 1 percent. An alternative suggested by the cluster model of the solid solution is that a graded layer exists over several atomic planes at the interfaces. A chalcopyrite-like, ordered region at the interface would spread the strain change over the several layers and perhaps reduce the magnitude of the elastic strain in the layers. The gradation of strain, if present, would decrease the likelihood of damage of a strained superlattice by cracking or dislocation injection. It may be significant in connection with the ordered interface concept that strained superlattices have generally been made for pseudo-binary alloys, e.g., GaAs-Ga (P,As), rather than those with more components where an ordered structure would be less stable. A second possible phenomenon is associated with the absence of order with

$\Delta a/a = 0.07$ in the $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$ alloy but its presence with $\Delta a/a = 0.10$ in the $\text{Ge}_{0.5}\text{Cd}_{0.5}\text{As}$ alloy. This result implies that the entropic term favoring disorder dominates the strain energy term favoring order in the (Ga,In) As alloy grown at the melting temperature. If the latter alloy could be grown at a lower temperature where the entropic contribution to the free energy of the solid is less, an alloy with increased order, perhaps even with the chalcopyrite structure, could form. A possibility in this regard would be to form an amorphous $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$ alloy and then to crystallize it just above the glass transition temperature.

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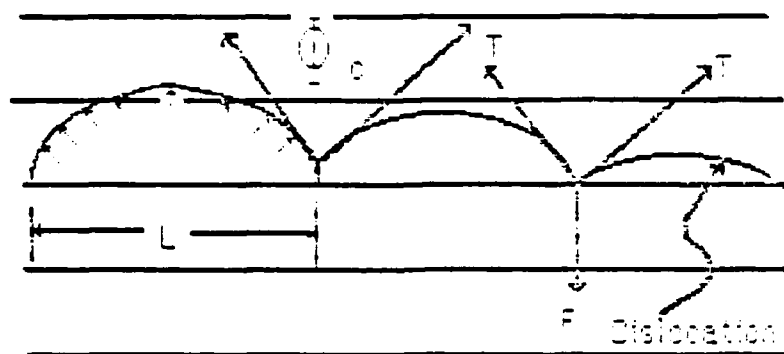


FIG. 1. Glide plane geometry showing a dislocation bowed-out to a critical configuration just about to break away from solute pinning points at spacing L . The solute pinning force F is balanced by resolved line tension forces T and in turn by the force $\sigma_c b L$ associated with the distributed force per unit length $\sigma_c b$ of the resolved applied stress.



FIG. 2. Typical flow stress-temperature plot for a metal solid-solution alloy.

ANALYSIS OF THE POTENTIAL OF A REDUCED GRAVITY ENVIRONMENT FOR GROWTH OF ELECTRONIC MATERIALS

A. F. Witt

The potential of a reduced gravity environment can be assessed when considering the nature and origin of existing deficiencies in materials grown from the melt in a conventional 1g environment.

All melt growth configurations require the establishment of thermal gradients (across the growth interface) which are destabilizing in a gravitational field. A consequence is the occurrence of buoyancy drive convection which is turbulent in industrial growth geometries. Turbulent convection in multi-component melt systems (conventional electronic materials) during growth results in:

- (a) Axial and radial macrosegregation;
- (b) Microsegregation;
- (c) Non-equilibrium point defect formation.

Convection results in:

- (d) Enhanced dissolution of crucible materials (contamination).

Convective heat transfer in the melt limits our ability to establish steep thermal gradients across the melt interface and thus, in many systems of concern, gives rise to:

- (e) Constitutional supercooling and related growth interface breakdown.

As indicated in a preceeding workshop report, the listed side effects of turbulent convection constitute the primary obstacles to the achievement of chemical uniformity and crystalline perfection in crystals grown from melts and high temperature solutions. All efforts to suppress convective melt

flows in conventional growth configuration have so far been unsuccessful. The application of magnetic fields (vertical and horizontal) has been found to result in a suppression of thermal instabilities in highly conductive melts (turbulent convection changes to laminar convection), but is found to be ineffective in associated melts (CdTe and oxides). In all instances, macrosegregation is only marginally decreased, residual convective melt flows are pronounced.

Given this background, consideration of growth in a "zero" gravity environment becomes extremely attractive. This attractiveness is in principle decreased by:

- (a) The magnitude of residual g forces in available orbital configurations (g values range from 10^{-3} to 10^{-5});
- (b) g-level perturbations due to corrective rocket firing (g-jitter);
- (c) Man-made perturbations in orbiting vehicles.

Most importantly, the effects of forces other than buoyancy on mass transport have to be considered. Dominant among these is surface tension driven convection (Marangoni flows) and bulk mass transport due to volume changes associated with liquid-solid phase transformation.

The magnitude of residual convective flows in low g environment can as yet not be quantitatively assessed, primarily because of the unavailability of required $d\sigma/dT$ and $d\sigma/dc$ data. Also unassessable at this time is the effect of the residual convective flows on crystalline and chemical perfection associated with growth from the melt. For example, on the basis of available data, it was predicted that in a 10^{-4} g environment, unconfined growth of doped InSb and Ge would be controlled by Marangoni-type flows

expected to be equal in magnitude to buoyancy driven flows in a 1g environment.

An analysis of the crystals grown in orbit indicated the total absence of microsegregation inhomogeneities and provided no evidence for any convective interference with growth and dopant segregation. The suggested explanation of the experimental findings invoked the existence of a coherent oxide film on the melt surface (related shear forces are assumed to have resulted in a suppression of noticeable convective bulk flows).

The limited number of experiments conducted in space showed that the build-up of solute boundary layers with considerable thickness, associated with growth, renders radial macrosegregation extremely sensitive to the morphology of the growth interface. The absence of radial segregation becomes contingent on the establishment of a planar growth interface morphology. These growth experiments revealed also that in a reduced g environment the wetting behavior between the melt and the confining crucible is different from that observed in a 1g environment and that in semiconductor systems it is sensitive to dopant additions. Ga-doped Ge and Te-doped InSb were observed to be non-wetting in confining quartz ampoules, and the material grown in space could be removed manually from the ampoules. Sn material grown in space could be removed manually from the ampoules. Sn-doped InSb was found to wet the confinement and after growth could only be secured after dissolution of the quartz ampoule. It should be pointed out that non-wetting configurations are of extreme interest since they are a prerequisite for defect free confined growth and, for obvious reasons, result in minimum contamination of the melt.

The limited experimental data on growth in a reduced gravity

environment do not permit a reasonable assessment of its potential for growth of electronic materials, nor does the available theoretical framework. The growth behavior in reduced gravity environment can only be assessed following extensive experimentation in space.

Considering the failure of all efforts to suppress, during growth on earth, the adverse effects of buoyancy driven convection, it is recommended to conduct in space some well designed growth experiments with systems in which the application of magnetic fields for the reduction of convective interference fails (for example, CdTe, $\text{Bi}_{12}\text{SiO}_{20}$). Such experiments can assist in clarifying the relationship between convection and the formation of non-equilibrium point defects, considered a primary obstacle to the achievement of theoretical materials properties. Such experiments can also be used to achieve multi-component systems of compositions not yet attainable on earth because of constitutional supercooling effect. For oxide systems, the possibility exists to establish non-wetting configurations and thus to avoid detrimental crucible contamination.

Taking into account the magnitude of matrix deterioration resulting from interference of buoyancy driven convection with crystal growth and segregation and our inability to suppress or circumvent this phenomenon in a 1g environment, it is recommended to explore the usefulness of low g environment. Related R&D activities should in first line focus on a clarification of the relationship between gravity driven convection and defect formation. Although considerations of possibly utilizing space for growth of strategic electronic materials for device fabrication should not be excluded a priori, these considerations should not, however, dictate the nature of this exploratory effort.

MATERIALS PROCESSING IN SPACE

J. L. Margrave

Proposals for materials processing in space which offer unequivocal scientific, engineering or economic advantages over processing the same materials on earth have been scarce. Obviously, one must either achieve a level of crystalline perfection, a level of chemical purity or a unique stoichiometry in a product in order to add enough value to justify the expense of space processing of a material which is sent up, processed and then returned to earth. Somewhat different criteria will apply if a material (object) is to be fabricated and used in space. Thus, techniques for space processing of very large plastic, glass or metal spheres in space will be needed to construct a space station. Prototype small-scale experiments will provide background insight. One predicts that a "molten" glob of glass, plastic or metal could be blown to form a rigid perfect sphere in the micro-gravity environment, but how will such bubbles deteriorate in the UV-photon flux of high altitudes, how permeable will modest wall thicknesses be to prevent escape of O_2 , H_2O , CO_2 and similar gases, just how big a bubble can be utilized to house a "space colony" of food plants, of bees or perhaps an orbiting "biotron" containing plants and animals and people.

As structural members of a space building, prepared in space, one can undoubtedly utilize many shapes and materials -- hollow tubes, rods, sheets, fiber-reinforced composites, etc. -- ranging from plastics to glasses to metals. In the absence of gravity, architectural designers will be liberated from load-bearing limitations and in the absence of atmospheric wind effects very extensive (area and height) structures are feasible.

Another suggestion for developing a space-processing technique would be an experiment designed to see how long (and how fine) one could draw a

plastic or glass fiber from a melt. A very thin continuous straight fiber could be a useful optical fiber. If ten or one-hundred were drawn simultaneously and twisted, they could make a continuous cable which was miles long.

Another direction to pursue in space-processing or materials involves materials which are poor performers on earth because of chemical problems in the presence of air or water, yet which possess good mechanical, thermal and structural properties. For example, very active metals like the rare earths, their carbides, borides, etc., could be useful in space.

More practical in space or on the moon than it is on earth would be the polymeric solid $(\text{SiF}_2)_x$, the silicon analog of teflon. It is tough and generally similar to teflon except for its reactivity with O_2/N_2 in air to form SiO_xN_y and its even more exothermic interaction with water. Since silicates are common on the moon, one could utilize NaF (or HF) to produce SiF_4 and then SiF_2 by reduction to yield "moon-teflon" -- $(\text{SiF}_2)_x$ -- a material uniquely useful in space.

In summary, materials processing techniques in space can make creative use of the unique parameters of the space environment:

- (1) Micro (or at least, milli-) gravity
- (2) Free photons, including the vac. uv
- (3) Reasonably good vacuum
- (4) Electricity from photovoltaic devices
- (5) Solar heating if desired
- (6) Low ambient temperature
- (7) Absence of O_2 and H_2O as corrosive cases

STRUCTURE AND PROPERTIES OF SOLID INTERFACES RELEVANT TO ELECTRONIC MATERIALS: OVERVIEW

H. Ehrenreich, J. P. Hirth and T. C. McGill

A workshop under this title was held on July 11-13, 1984, the agenda and list of attendees is attached. Its conclusions are surprising: Practically every semiconductor heterojunction interface has been inadequately characterized with respect to its morphology, chemical composition, and its mechanical and electrical properties. The theoretical understanding is equally poor. Calculations for the band off-sets do not include a self-consistent treatment of the electronic effects, nor the effects of dipole layers arising from atomic and charge distributions at the interface. Metal-semiconductor interfaces, i.e. ohmic contacts and Schottky barriers, still possess many features that remain to be understood both experimentally and theoretically. Strained superlattices are potentially important, but have not yet received sufficient attention with respect to stability and reproducibility. The polymer-metal interface represents an extremely important problem area, about which the MRC hopes to hear more next year. The tunneling microscope is likely to have a considerable impact on this field in clarifying the details of surface structures and the morphology of monolayer and submonolayer structures.

The application of experimental techniques developed in metallurgy to semiconductor systems could be potentially very important. Such techniques extend from mechanical testing to investigations of chemical decoration of interface.

AGENDA

STRUCTURE AND PROPERTIES OF SOLID INTERFACES RELEVANT TO ELECTRONIC MATERIALS

Materials Research Council
Torrey Pines Elementary School
La Jolla, California

July 11-13, 1984

WEDNESDAY, July 11

Atomic Structure of Interfaces, Chairman: J. P. Hirth

Formation of Interfaces: Ludeke, IBM
Thin Film Nucleation and Growth: Moazed, N. Carolina St.
Dislocation Structure: Vaudin, Cornell
Surfaces, Interfaces and Defects: Tiller, Stanford

Atomic Transport and Chemical Reactions, Chairman: R. Mehrabian

Segregation: Briant, GE
Transport of Interfaces: Tu, IBM
Reaction Layers of Metallic Interfaces, e.g., Pd-Si: Lau, UC
San Diego
Passivation Kinetics: Wieder, UC-San Diego

THURSDAY, July 12

Electronic Structure: Experiment, Chairman: T. McGill

Band Offsets: Bauer, Xerox
Schottky Barriers and Metal-Semiconductor Contact:
Spicer, Stanford
Tunneling Microscopy: Foster, Stanford
Transmission Electron Microscopy: Petroff, Bell

Layered Structures and Theory, Chairman: G. Vineyard

Layered Structures
Strained Superlattices: Osbourn, Sandia
Modulated Metallic Structures: Clapp, Univ. Conn.
Theory: Hamann, Bell

FRIDAY, July 13

Future Prospects: Devices & Research, Chairman: H. Ehrenreich

Surface Science of Polymeric Adhesion: Dwight, VPI
Future Prospects: Armstrong, IBM; Wernick, Bell

Informal Discussions

ATTENDEES

Structure and Properties of Solid Interfaces Relevant to Electronic Materials July 11-12-13, 1984

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ELECTRONIC PROPERTIES OF INTERFACES

T. C. McGill and D. K. Ferry

Two of the key parameters in the design and function of any solid state electronic device are the relative position of the electronic levels across an interface and the ability of the interface to support or inhibit an electric current. Examples of the relative position of key electronic levels include: the position of the Fermi level in the metal with respect to the valence or conduction band edges of the semiconductor immediately inside the semiconductor (the Schottky barrier) and the relative position of the conduction and valence band edges in the semiconductors across a heterojunction interface (the band offsets). The ability of an interface to pass electric current with a minimum potential drop is the key to making a successful ohmic contact.

The importance of these parameters may be judged by observing the manner in which they appear in some important devices. The value of the Schottky barrier primarily determines the performance of the metal-electrode-field-effect transistor, as it is the controlling electrode for these devices. In high electron mobility transistors, the band offsets strongly affect the number of carriers that are confined in the notch between the doped GaAlAs and undoped GaAs. The band offsets are also the key parameter in determining the improvement in performance of heterojunction bipolar transistors. The performance of ohmic contacts are found to be a limiting factor for high-density, high-speed device technologies.

Because these parameters are key to continued development of advanced semiconductor devices, it is reasonable to inquire as to where we

stand on the measurement and prediction of these very important parameters.

CURRENT STATUS

Schottky Barriers

The current status of Schottky barriers is that we have fairly good experimental techniques for obtaining the values of the barrier itself, a posteriori. However, we do not have a complete understanding of the parameters governing the values of the Schottky barrier for a given metal-semiconductor system. One of the major questions is still the origin of the so-called Fermi-level pinning. For most semiconductors, the Fermi level of the metal is pinned at a relatively specific value in the semiconductor band-gap, independent of the properties of the metal. One suggestion for the origin of this pinning phenomenon is that intrinsic interface states act as a receptacle of the charge from the metal and hence form a dipole layer between the semiconductor and the metal. This dipole layer adjusts to the appropriate size required to fix the Fermi level position. Another important concept introduced by Professor Spicer (Stanford) is the suggestion that defects formed on the semiconductor side of the interface could become charged and act as one sign of the charge in the dipole layer. Again this dipole layer adjusts to fix the Fermi level. While both of these concepts have a multitude of supporters, who each claim that their model explains a major part of the problem, it is still not possible at the present time to show that one of the models is correct and that the other is not. The defect model has been successful in accounting for a large range of experimental data.

While theories of Schottky barriers have been pursued by almost every major solid state theorist, none of the theories are capable of giving a first principles prediction of the barrier height. The inherent difficulty for the theorist is having to deal with a situation that lacks translational invariance and has unknown morphology. This makes it unlikely that a complete theory will be presented in the near future. Even in the more restricted case where translational invariance is valid and the structure is thought to be known, first principles calculations have resulted in values for the Schottky barrier that are in disagreement with those observed in experiment.

Band Offsets

Band offsets are in a more unsatisfactory state. Until recently, the best accepted band offset was that for the GaAlAs-AlAs system. Measurements of the band offsets in heterojunctions of these materials led to the well-known 85/15 rule which stated that 85% of the difference in band gap was taken up in the conduction band offset and 15% was taken up in the valence band offset. This has become known as Dingle's rule. This rule has been used for a number of years to interpret most of the results for such heterojunctions. However, recent experimental results have appeared which are claimed to be in substantial disagreement with the Dingle rule. These would indicate that a more appropriate breakup of the band gap between valence band and conduction band might be 60/40. This represents a big change from the Dingle rule. However, analysis of the arguments leading to these conclusions by the current authors indicate that the experimental results may not form a sensitive test for the band offsets. The current situation is very confused and will require both careful

experiments and further analysis of data to obtain good values of the band offsets.

In recent years, Bauer and co-workers (Xerox, PARC) have shown that processing can change the value of the band offset. While, in principle, this observation could be the basis for obtaining tailored offsets, the results so far do not indicate that band offsets can be tailored or that they can be controlled in such a way as to make the tailoring suitable for a manufacturing process.

Many theories have been put forward to explain the values of the offset and to assist in the projection of values for new heterojunction systems. Some of the more successful of these theories include: The common anion rule and the empirical tight binding theory of band offsets. The common anion rule states that if there is a common anion on either side of the interface, then the valence band offset will be small and most of the band gap difference will appear as an offset in the conduction band edge. This concept would hold in the case of the Dingle rule. Another success for this concept is the HgTe-CdTe heterojunction, where the valence band offset is thought to be very small (about 40 meV). The empirical tight binding theory of band offsets states that one can obtain the valence band offset by taking the difference between the positions of the valence band edges of the constituent materials when these are referenced to some vacuum level. This theory has also had a number of successes and is capable of giving results for cases in which the common anion rule is not appropriate. None of the theories explicitly deal with the problems presented by the interface. Both are based on the idea that there is no dipole layer at the interface.

Ohmic Contacts

Ohmic contacts are one of the least understood pieces of modern device technology. The problem of the ohmic contact is to overcome the natural tendency of metal-semiconductor interfaces to be a rectifying contact. To produce a contact that has a low resistance, a number of layers of material are applied to the semiconductor and this multi-layered structure is heated to produce a metallurgical reaction. Ohmic contacts have been produced by using molecular beam epitaxy but, it is not clear whether these will find broad application in device technology.

CONCLUSIONS

Given the relatively unsatisfactory situation, after a great many years of work, one might be tempted to question further work on this subject. However, the problems of Schottky barriers, band offsets, and ohmic contacts are too important to neglect a continued search for a first principles understanding of their behavior. Progress is continually being made in developing knowledge of these crucial phenomena. Hence, we feel that this area is important for continued development. Some of the major areas that we feel could profit by attention are:

- Careful experimental studies on prototype systems. The systems should be prepared in a controlled ultra-high-vacuum environment. The experimental measurements should address key issues of the electrical and morphological properties of the interfaces. Both standard surface analysis techniques as well as electrical measurements should be used.

- Theoretical work in the area of testing the limits of validity of various models of Schottky barriers, band offsets, and ohmic contacts would be encouraged. Close coordination between the theory and experiment will be required to access the meaning of various experimental results in terms of the basic chemistry and physics of the interfaces.

ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION

R. J. Gutmann

In the epitaxial growth of compound semiconductors with close control of thin layers, conventional wisdom states the following:

- 1) Use molecular beam epitaxy (MBE) to do basic science and fabricate exploratory device concepts.
 - 2) Plan on using organometallic chemical vapor deposition (OMCVD) for eventual production of discrete devices and integrated technologies.
- This conventional wisdom is based upon MBE being capable of monolayer control in a good vacuum environment with appreciable surface science instrumentation capabilities, albeit with low throughput potential. However OMCVD needs a strong research base to delineate the capabilities and limitations of this epitaxial growth technique and to develop a technology base that will allow extension to production in the future.

This section of the report presents an overview of the status of OMCVD in III-V growth for microwave and optical devices and circuits and II-IV growth for infrared applications. In particular the discussion is restricted to GaAs, GaAlAs/GaAs, GaInAs on InP and HgCdTe. The issues to be addressed can be divided as follows:

- starting materials
- reactor design
- growth mechanisms and in-situ diagnostics
- effluent control

It should be realized that as one proceeds from GaAs to GaAlAs/GaAs to GaInAs on InP to HgCdTe that the experience base is reduced and the basic research required is increased.

Starting Materials

Many of the starting materials for OMCVD are supplied by small companies without research laboratories so that purity and consistency could be expected to be of concern. With GaAs, trimethyl gallium appears to be reasonably well controlled while triethyl gallium has received less work and appears less satisfactory. The key problem at this point appears to be arsene with water vapor, oxygen and possibly metallic (e. g., zinc) contamination. A recently developed technique is to bubble the arsene through a ternary melt of In-Ga-Al (liquid at room temperature) to remove oxygen and water. Triethyl indium and trimethyl indium considerations are less well documented and results appear more inconsistent. It is clear that additional gas purification is desirable before OMCVD is a production process, particularly for high performance microwave devices and high efficiency optical devices which can be sensitive to deep levels such as carbon.

Reactor Design

There are an appreciable number of factors in OMCVD reactor designs but two key issues are low pressure (LPOMCVD) versus atmospheric pressure and single wafer versus multiple wafer capability. Atmospheric reactors are more widely used and are suitable for high quality relatively thick (>0.1 microns) layers. However, in growing high electron mobility transistors (HEMTs) or superlattices layers 50Å to 200Å layers are needed, with sharp boundaries having monotonic gradients in composition and doping. Shut off transients, even with equalized pressure bypass lines, are limiting factors in atmospheric reactors, although success has been reported by direct gas injection in vertical reactors. LPOMCVD (actually reduced

pressure CVD since the pressure is ~ 0.1 atmosphere) is more compatible with sharp but monotonic interface gradients. However, there is less experience with such reactors.

Most research reactors have single (or, at most, a few) wafer capability. Production reactors with ten to twenty 2" diameter wafer capability are becoming available but the uniformity and reproducibility have yet to be demonstrated. For example, a single wafer research reactor may exhibit $\pm 10\%$ control on epi layer thickness and doping concentration, with $\pm 4\%$ being reported in some laboratories. The control exhibited in HEMTs or superlattice structures is not readily available, but there are reasons to expect comparable variations if the transient growth gradients can be maintained.

Growth Mechanisms and In-Situ Diagnostics.

There has been significant advances in the growth of compound semiconductors with OMCVD in the last decade. However, the basic growth mechanisms are not well understood and current emphasis on new device structures and new compound semiconductors has not been compatible with fundamental investigations. In particular OMCVD reactors have not been well instrumented with in-situ diagnostics that would assist in basic understanding of the chemical reactions. There is a need to better understand the basic chemical reactions and the surface chemistry of epi growth. This would appear to be a key area for research support, although the desirable in-situ diagnostics need to be defined.

Furthermore, the subject of optical assisted growth appears desirable for investigation. Both flood beams to possibly lower substrate

temperature requirements and focused beams for selective area growth could be desirable. Lack of previous research in these areas appear limited by the small number of researchers in OMCVD and the desire to fabricate layers, test structures and devices with performance close to MBE.

Effluent Control

The safety issue of OMCVD remains a concern, both the handling of toxic materials during processing and control of effluents. While baffling and filtering techniques have been developed in various laboratories, it is important to realize that production standards may be more stringent than in a research environment. Also, LPOMCVD requires higher arsenic to gallium ratios and therefore more arsenic effluent, so that atmospheric pressure reactor effluent design may not be sufficient.

Summary

In summary, OMCVD has demonstrated the ability to fabricate new device structures, although in general with somewhat inferior performance compared to MBE. However it is clear that OMCVD is a promising (if not the most promising) growth technique for future production of HEMTs and superlattice devices and related integrated circuits. There is much research to be performed, in particular:

- in-situ diagnostics of OMCVD epi growth to improve our understanding of chemical reaction mechanisms.
- reactor design to control compositional and doping concentration interface gradients.
- starting materials, both purity of present materials for better reproducibility and new materials for lower temperature growth.

These three recommendations are given in decreasing order of priority.

References

Previous knowledge of OMCVD and MBE.

Presentation of R. D. Burnham at MRC Meeting.

Conversations with T. McGill and D. Ferry at MRC Meeting.

Telephone conversations with S. K. Ghandhi (RPI), R. Bhat (Bell Communications Research) and D. Reep (GE).

Brief Conversations with D. Dapkus (USC) and R. Milane (Rockwell) at Optical Interconnect Meeting.

EDGE CRACKING OF MULTILAYER STRAINED SUPERLATTICES

A. G. Evans

Elastic layers subject to lattice strain of alternating sign (Fig. 1) induce substantial shear stresses, at the interface, in the vicinity of the layer terminations. These shear stress can cause cracks to propagate in from the ends and, in some cases, induce delamination. The magnitude of the stresses and of the stress intensity factor associated with edge cracks are calculated and used to predict trends in cracking with layer thickness and strain.

The shear stresses can be calculated by imposing edge traction (Fig. 1) of magnitude

$$\sigma = \pm E\epsilon/(1-\nu) \quad (1)$$

where ϵ is the lattice strain, E is Young's modulus and ν is Poisson's ratio. (These stresses superpose on initial, in-plane normal stresses of magnitude, σ . Note, however, that, for alternating layers of equal thickness and constant strain amplitude, there are no normal stresses at the interfaces.) The edge tractions give the stresses,

$$\sigma_{xy} = 4z^2\sigma/\pi \int_0^h x dx/(x^2+z^2)^2 \equiv 2E\epsilon h^2/\pi(1-\nu)(z^2+h^2) \quad (2)$$

where Z is the distance from the end and h is the layer thickness.

The shear stresses include a mode II stress intensity factor,

$$K_{11} = 4Eh^2\lambda/\pi^{0.56}(1-\nu)a_0\int^a dz/\{1-(z/a)^2\}^k : k = (z^2+h^2) \\ = 2E\epsilon h\lambda/[\sqrt{\pi}](1-\nu)\sqrt{a}(\ell); \ell = (1+h/a)^2 \quad (3)$$

which can be re-expressed in the dimensionless form

$$(1-\nu)K_{11}/E\epsilon\sqrt{h} = 2\lambda(h/a)^{0.5}/\{(\pi)^{0.5}\}^k ; K=(1+h/a)^2 \quad (4)$$

where λ is a constant ≈ 2 . This function exhibits a maximum, at $h/a=1/3$, given by:

$$(1-\nu)K_{11}/E\epsilon\sqrt{h} = 3^{3/4}\lambda/2\sqrt{\pi} \quad (5)$$

Since the materials are brittle, the K_{11} is transmitted to the tip of an edge crack and causes crack extension when a critical value, K_c , has been exceeded. Here, by equating K_{11} to K_c Eqn. (5) may be used to establish a condition for which edge cracking is prohibited: notably,

$$h = 4\pi(1-\nu)^2K_c^2/3\sqrt{3}(E\epsilon)^2\lambda^2 \quad (6)$$

Inserting some typical values for the materials of interest ($K_c \approx 5 \times 10^5 \text{ MPa}\sqrt{\text{m}}$, $E=200 \text{ GPa}$, $\epsilon=10^{-2}$, $\nu = 1/4$), the critical film thickness, h_c , below which cracking cannot occur is, $h_c \approx 2 \times 10^{-8} \text{ m}$. Hence, the films must exceed about 250\AA in thickness before edge cracking becomes a serious concern (assuming that the properties selected are, indeed, typical).

This preliminary calculation indicates that films with a thickness

at the envisaged upper limit are susceptible to edge cracking. Hence, more detailed calculations and the associated experiments seem justified. Finally, it is emphasized that the effect discussed here is exclusively related to residually stressed films, with alternating character. Similar effects would not be encountered in unstressed systems.

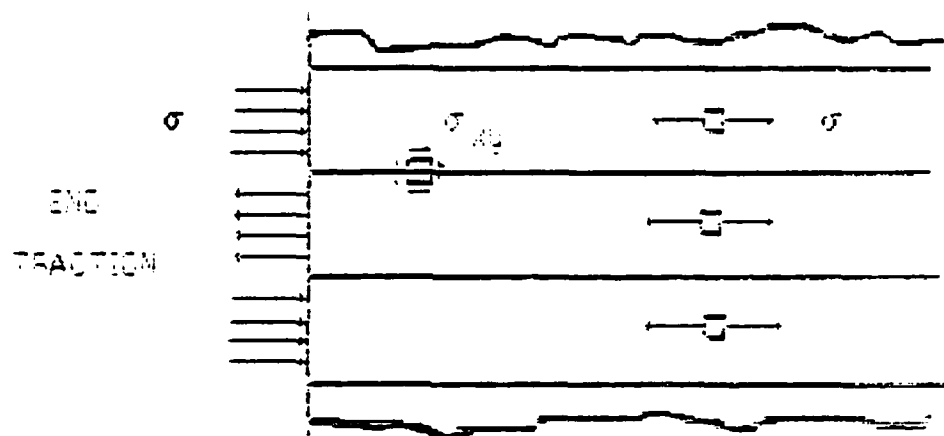


FIGURE 1.

DAMAGE OF STRAINED SUPERLATTICES BY DISLOCATION INJECTION

J. P. Hirth

INTRODUCTION

Strained superlattices of lattice-mismatched compound semiconductors have been grown by Osbourn and co-workers¹ and by Blakeslee and co-workers² and their electronic properties studied. The layered structures can be grown dislocation-free when the layer thickness h (Fig. 1) is less than a critical thickness h_c first discussed by Matthews and Blakeslee³. With crystals such that the lattice parameter a_B of B is greater than that a_A of A, the relaxed misfit, cross-grid, dislocation array will be that of Fig. 1. An issue of interest at the meeting was whether a strained superlattice is stable against damage. We address the possibility of damage in the form of dislocation injection by glide or climb. To provide background we first briefly reviewed the Matthews and Blakeslee theory. We treat the case where the dislocations are perfect, but the equations can be directly adapted for other examples.

Consider the configuration of Fig. 2. The dislocation is that of Fig. 1 with Burgers vector $\underline{b} = (b; 0, 0)$. Spreading of the dislocation in the x direction involves creation of the dislocations with an accompanying energy changes

$$W_1 = \{2\mu b^2 L / 4\pi(1-\nu)\} \ln(h/b) = \{\mu b^2 L / 2\pi(1-\nu)\} \ln(h/b) \quad (1)$$

Where μ is the shear modulus, ν is Poisson's ratio, and $(\mu b^2 / 4\pi) \ln(h/b)$ is the line tension or energy per unit length of the edge dislocation⁴.

The dislocation pair releases elastic strain energy per unit length in an area $2\lambda h$ in Fig. 1. Since b is proportional to the lattice parameter the spacing $1)$ in a relaxed layer is related to $\Delta b = b_B - b_A$ by

$$\lambda/b = b/\Delta b = a/\Delta a \quad (2)$$

where to first-order one can take either $b = b_A$ or $b = b_B$. The biaxial strain is such that

$$\epsilon = \epsilon_{xx} = \epsilon_{yy} = \pm \Delta a/2a \quad (3)$$

where the + or - applies to layer A or B, respectively.

The accompanying strain energy per unit volume is

$$W = \mu \epsilon^2 (1-\nu)/2(1-\nu) \quad (4)$$

Thus, spreading of the dislocations releases strain energy

$$\begin{aligned} W_2 &= 2\lambda h L \mu \epsilon^2 (1+\nu)/2 \\ &= \{h L \mu (1+\nu)/4\} \Delta b/b \end{aligned} \quad (5)$$

The condition for spreading of the loop is that $W_1 - W_2 < 0$ which occurs for $h > h_c$ with h_c determined by the condition $W_1 = W_2$ or

$$b/h_c \ln(h_c/b) = \{\pi(1+\nu)/2\} \Delta b/b \quad (6)$$

Typical values of h_c for compound semiconductors are 30-40 nm. Use of anisotropic elastic theory can change this value by up to 30 percent. The theory³ usefully predicts that a base layer with $h > h_c$ should pinch-off dislocations with components b_x or b_y as illustrated in Fig. 3. Further layers with $h < h_c$ can then be grown under conditions where nucleation of dislocation loops of the type in Fig. 6 requires stress activation and hence where layers can be dislocation-free as observed^{1,2}. Moreover, even with stress activation of a dislocation, such as $1/2 [101]$, with a b_x or b_y component, following growth, the energetics favor trapping of the loop in the first layer as shown in Fig. 4.

DISLOCATION DAMAGE

Nucleation of a semicircular dislocation loop at the surface of a homogeneous, single phase material requires a stress⁴.

$$\sigma = S^2/40bkT \quad (7)$$

Where S is the dislocation line tension, k is Boltzmann's constant and T is absolute temperature. Typically σ is of the order of 0.01 to 0.05 μ . Such stresses can only be achieved under severe stress concentrations at low temperatures where glide is dominant. At elevated temperatures the necessary stress is reduced for glide and becomes achievable also for climb nucleation which could be enhanced by thermodynamic driving forces associated with interdiffusion.

For the layered structure, the effective line tension for the process in Fig. 5 is related to W_1 and W_2 ,

$$S = \{\mu b^2/4\pi(1-\mu)\}\ln R/b - \{\mu b^2(1+\nu)/4\}h\Delta b/b^2 \quad (8)$$

Here $R = \mu b/\sigma$ for the first loop, while as the array approaches that of Fig. 1, $R = h$. At $h = h_c$, S is negative for $R \leq 5.3h$ and dislocation loop nucleation of the type shown in Fig. 5 is spontaneous. For smaller values of h a barrier for nucleation is still present.

For the single-phase case, Eq. (8) applies but with the second-term on the right side being absent. Thus, compared to the single-phase case, the dislocation nucleation in Fig. 5 is always easier, with the reduction in S being linear in both layer height h and relative lattice mismatch $(\Delta b/b) = (\Delta a/a)$. Similar considerations would apply for nucleation of the type in Fig. 5 if the Burgers vector were to have components b_x and b_y . If the Burgers vector has only a b_z component, nucleation in a layered or single-phase material would be equally likely.

The continued propagation of dislocations, once nucleated, would depend on the slide constraint of a friction force or Peierls barrier⁴. In III-V compound semiconductors it appears that the magnitude of the Peierls stress is such that propagation should not occur at room temperature. However, for III-V compounds at elevated temperatures or for II-VI compounds at room temperature and above, layered structures are vulnerable to damage in the form of dislocation injection.

CONCLUSIONS

1. Dislocation nucleation is easier in layered structures than in single phase structures.

2. The critical stress for nucleation depends quadratically on a factor S that decreases linearly with layer spacing λ and lattice mismatch Δa .
3. Dislocation propagation should be suppressed in III-V compounds at room temperature, but III-V compounds at elevated temperatures or II-VI compounds at room temperature and above are vulnerable to damage by the nucleation and propagation of misfit dislocations by glide or climb processes.

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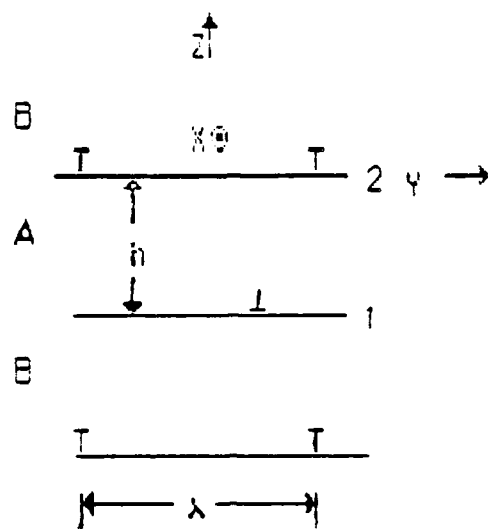


Figure 1. Dislocations in strained superlattices.

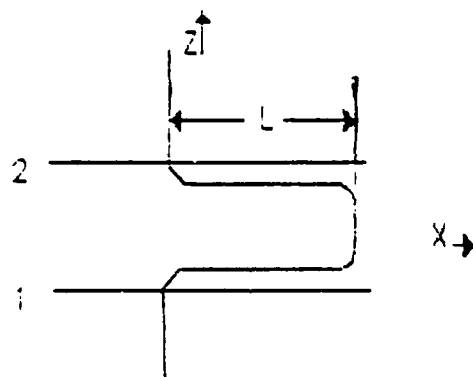


Figure 2. Spreading of dislocation 1-2 in Fig. 1.

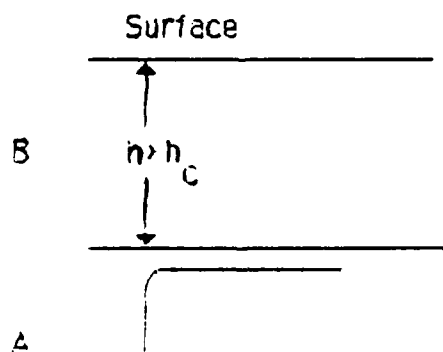


Figure 3. Pinch-off of dislocations at surface.

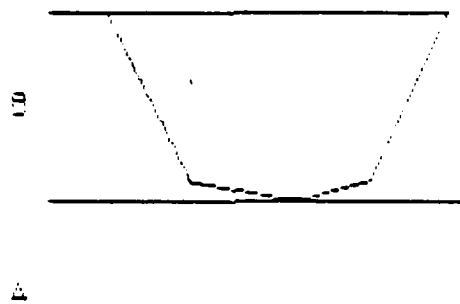


Figure 4. Trapping of dislocations near surface.

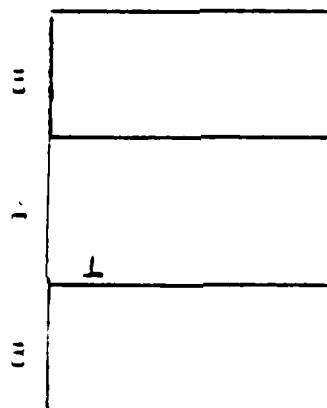


Figure 5. Nucleation of dislocation.

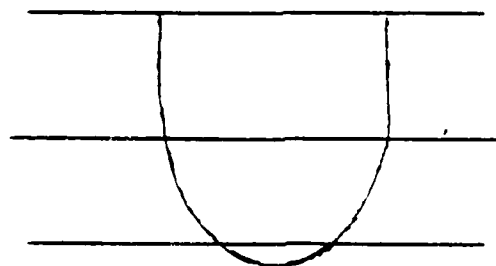


Figure 6. Nucleation of dislocation loop at surface.

EPITAXIAL METHODS FOR PREPARING THIN SEMICONDUCTING LAYERS

R. Gutmann, T. C. McGill, D. K. Ferry, and R. N. Osgood

INTRODUCTION

Many of the new electron device concepts depend on the preparation of thin epitaxial layers of electronic grade semiconductor materials. Growth of these thin layers can be achieved from liquid or vapor. Liquid phase techniques have been explored extensively and are currently used for production of a number of optoelectronic devices. However, growth from the liquid phase means that the solid must be in contact with a rather high temperature melt. The high temperatures of the solid results in interdiffusion of various layers, leading to non-abrupt interfaces. To circumvent this problem with liquid phase epitaxy, two forms of vapor phase epitaxy have been receiving wide attention. These two methods are called molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). In MBE the substrate is contained in an ultra-high-vacuum system and the layer is grown from material supplied by either molecular beam or evaporation sources. In CVD growth, the material to be deposited is supplied by vapors of chemical compounds containing the appropriate atoms. These compounds are thought to react at or near the substrate where the deposition is to take place. One of the most widely studied methods for depositing semiconducting layers now uses metal-organic compounds and hence is called MOCVD.

Both of these techniques, MBE and MOCVD, have been extensively used for making semiconducting layers for devices. MOCVD and MBE have been used to fabricate various opto-electronic devices, including structures requiring sharp interfaces. MBE has been particularly successful in the growth of various high speed electron device structures, including the

high-electron-mobility field-effect transistor (HEMT) and other structures. The potential of MOCVD for producing electronic devices is now being explored and a French group has recently reported the fabrication of HEMT's using MOCVD techniques. Both of these techniques are uniquely suitable for certain material systems. For example, phosphorus-based semiconducting alloys are more easily grown by MOCVD, while MBE has been more successful in obtaining high quality material in the HgCdTe system.

Major efforts in these materials production technologies are being carried out by groups outside the U.S. Much of the recent research successes in MOCVD and MBE have been coming from abroad, as the French and the Japanese both have very successful programs in MBE and MOCVD. In fact, in a number of the key areas, they are the clear leaders. Their work is characterized by a basic approach rather than the predominantly engineering approach that drives most of the programs in this country.

OVERALL ASSESSMENT

At the present time there is no clear advantage to choosing either MOCVD or MBE for any of the materials systems where the two techniques can both produce layers. MOCVD has apparent advantages in production environments, while MBE is more compatible with surface analysis techniques and could produce a higher purity layer. Hence we suggest a balanced approach in which both are funded adequately to develop a fundamental understanding of the processes and their limitations. In the section below, we have detailed some problem areas that were identified by our three speakers in this area, R. Calawa (Lincoln Laboratories), J. Faurie (University of Illinois Chicago Circle) and R. D. Burnham (Xerox Palo Alto Research

Center). These were supplemented by brief discussions with other researchers in the community.

One might summarize the present feeling of the authors as believing that in the epitaxial growth of compound semiconductors with close control of thin layers:

- 1) Use molecular beam epitaxy (MBE) to do basic science and fabricate exploratory device concepts wherever possible.

- 2) Plan on using metal-organic chemical vapor deposition for eventual production of discrete devices and integrated technologies as well as fabrication of exploration devices. MBE is capable of monolayer control in a good vacuum environment with appreciable surface science instrumentation capabilities, albeit with low throughput potential. MOCVD has demonstrated a high level of achievement in optical devices. Moreover, a strong technology base is needed to allow extension to production in the future. MOCVD presents a more manufacturable thin-film technology for growth of thin modulated-doped structures than MBE, but is a molecular system in which it may be exceedingly difficult to control the precursor mixtures and concentrations.

MOLECULAR BEAM EPITAXY

Materials prepared by MBE can in principle be ultra-pure since it is thought that the contaminants could be removed to any arbitrary level. All of the tools of modern UHV materials preparation and diagnostics are consistent with this approach. The successes of MBE in producing some of the first HEMT electronics and superlattices has justified this position. However, MBE is not yet a production technology, even for the GaAlAs system where it has been extensively studied. Some of the major areas of research which

should receive more attention include: studies of new materials prepared by MBE, studies of the basic MBE process, studies of the defects that are formed during the growth process and methods for controlling their density, studies of scale-up of the processes and attempts to obtain uniform results.

Most of the work in this country has concentrated on the GaAlAs system. However, other systems could be of at least as great of interest. These include: HgCdTe system, other II-VI systems, Si compatible systems (SiGe and Si-silicides), III-V systems other than GaAlAs (for example GaInAsP and GaInAsSb systems). Each of these material systems could result in materials that could be the basis for major device innovations (this is true regardless of whether MBE or MOCVD is the growth mechanism).

The growth process in MBE is poorly understood even for the very well studied GaAlAs system. Some of the fundamental areas deserving attention include: the role of various chemical species on the surface during the growth process, the nature of the surfaces during growth, the development of a broad understanding of the fundamentals governing the growth process (is thermodynamics sufficient or is kinetics required), the physics and chemistry of the overall MBE systems including sources and the environment, which in spite of the UHV conditions does have background contamination by a number of chemical species. Finally, methods of spatially patterning the growth process are of interest for microelectronic applications.

Layers of GaAlAs grown by MBE are not currently defect free. They contain a unique class of defects: the so-called oval defects. While the areal density of these defects is quite variable and the cause has been the subject of a good deal of speculation, the precise origin of these defects is

not known. Thus there is no mechanism for eliminating them. As might be guessed the problem of defects in the layers has not been studied in any detail in other material systems.

Most of the MBE work is still at a laboratory scale where a few successes result in a published report. Laboratory scale is not likely to yield a product. In production, there is a need for high throughput, and *reproducible results*. While some of the laboratory results have been very exciting, the questions of scale-up and reproducibility are now questions that must be asked for the more mature systems such as GaAlAs.

METAL-ORGANIC CHEMICAL VAPOR DEPOSITION

Many of the starting materials for MOCVD are supplied by small companies without research laboratories so that purity and consistency are of concern. With GaAs, trimethyl gallium appears to be reasonably well controlled, while triethyl gallium has received less work and appears less satisfactory. The key problem at this point appears to be arsene contamination with water vapor, oxygen and possibly metal (e.g., zinc). A recently developed approach to solve this problem is to bubble the arsene through a ternary melt of In-Ga-Al (liquid at room temperature) in order to remove oxygen and water. Triethyl indium and trimethyl indium considerations are less well documented and results appear more inconsistent. It is clear that additional gas purification is desirable before MOCVD is a production process, particularly for high performance devices which can be sensitive to deep levels such as carbon.

There are an appreciable number of factors in MOCVD reactor designs, but two key issues are low pressure versus atmospheric pressure

and single wafer versus multiple wafer capability. Atmospheric reactors are more widely used and are suitable for high quality, relatively thick (0.1 microns) layers. However, in growing high electron mobility transistors (HEMT's) or superlattices, layers 5-20nm thick are needed. In addition, these layers must have sharp boundaries with monotonic gradients in composition and doping. Shut-off transients, even with equalized pressure bypass lines, are limiting factors in atmospheric reactors, although success has been reported by direct gas injection in vertical reactors. Low pressure reactors (actually reduced pressure CVD since there pressure is ~0.1 atmosphere) are more compatible with sharp but monotonic interface gradients. However, there is less experience with such reactors.

Most research reactors have single (or, at most, a few) wafer capability. Production reactors with capability for 10-20 2" diameter wafers are becoming available, but the uniformity and reproducibility of the wafers have yet to be demonstrated. For example, a single wafer research reactor may exhibit $\pm 10\%$ control on epi-layer thickness and doping concentration, with $\pm 4\%$ being reported in some laboratories. The control exhibited in layers for HEMT or superlattice structures is not readily available, but there are reasons to expect comparable variations if the transient growth gradients can be maintained.

There has been significant advances in the growth of compound semiconductors with MOCVD in the last decade. However, the basic growth mechanisms are not well understood and current emphasis on new device structures and new compound semiconductors has not been compatible with fundamental investigation of the process. In particular, MOCVD reactors have not been well instrumented with in-situ diagnostics that would assist in

basic understanding of the chemical reactions. There is a need to better understand the basic chemical reactions and the surface chemistry of growth. This would appear to be a key area for future effect, although the particular in-situ diagnostics need to be defined.

By properly equipping MOCVD systems with suitable optical diagnostics, it is possible to have very specific controls on reactants and, further, diagnostics that allow one to see and follow reactant intermediates evolved during the deposition process. For example, consider the growth of HgTe from Hg-atom vapor and gaseous dimethyl tellurium (DMTe). These reagents can be monitored by installing optical ports in the gas lines or CVD chamber and using tunable laser probes (The Hg atom concentration can be measured by using laser induced fluorescence at 254 nm). The DMTe concentration can be detected in the UV using a fixed or turnable UV laser in conjunction with a straight absorption measurement. In addition, it is possible to use an infrared diode laser to detect DMCD via a measurement of the vibrational lines at $3\mu\text{m}$.

In MOCVD systems, metal alkyls, such as dimethyl tellurium or dimethyl cadmium; are common precursor molecules. Despite the importance of understanding the precursor molecular chemistry to the growth of high quality epitaxial films, there is a surprisingly small body of knowledge on the structural properties, spectroscopy, or chemical purities of these materials. In addition, the spectroscopy of these materials in the infrared and ultraviolet is in many cases unknown.

An even more serious problem is the questionable purity of metal-alkyl molecules. Large and varying amounts of hydrocarbons often appear. Since these impurities have very different chemical properties than

the metal-alkyl precursors, their behavior in the CVD chamber is different and unexpected. This stray chemistry may not strongly effect the growth rate of the semiconductor, however, it could well lead to carbon contamination and defects in the CVD material.

Furthermore, the subject of optical assisted growth appears desirable for investigation. Both flood beams (to possibly lower substate temperature requirements) and focused beams (for selective area growth) could be desirable. Lack of previous research in these areas appear limited both by the small number of researchers in MOCVD and by the desire to fabricate layers, test structures, and devices with performance close to MBE. Along this line, recent results from Germany and the United Kingdom indicate that high-quality, localized deposition is possible.

The safety issue of MOCVD remains a concern, both in regard to the handling of toxic materials during processing and to the control of effluents. While the use of baffles and filtering techniques have been developed in various laboratories, it is important to realize that production standards may be more stringent than in a research environment. Low pressure MOCVD requires higher arsenic to gallium ratios and therefore more arsenic effluent. As a result, atmospheric pressure reactor effluent design may not be sufficient for these low pressure systems.

MOCVD has demonstrated the ability to fabricate new device structures. It is clear that MOCVD is a promising growth technique for future production of HEMT's and superlattice devices and related integrated circuits. However, there is still much research to be performed, in particular:

- in-situ diagnostics of MOCVD growth to improve our understanding of chemical reaction mechanisms.
- reactor design to control compositional and doping concentration interface gradients.
- Starting materials, both purity of present materials for better reproductibility and new materials for lower temperature growth.

FINAL COMMENTS

While the majority of the meeting dealt with the above mechanism, VPE has traditionally been used to prepare high quality material. Recently there have been indications from the Japanese and AT&T Bell Laboratories that it can be used to grow abrupt superlattice layers. Moreover, it is a process readily adapted to production environments. Clearly, some effort should be expended to evaluate the potential in this process for advanced materials.

Growth of Si by MBE and MOCVD could be of major technical interest. New device structures involving the SiGe systems and old device structures fabricated in thin epitaxial layers may become the standard Si device technology of the 1990's.

COMMENTS ON MO-CVD DIAGNOSTICS AND PRECURSORS

R. M. Osgood

1) It has been argued that MO-CVD presents a more manufacturable thin-film technology for growth of thin modulated-doped structures than MBE. A counter argument is that MO-CVD is an untidy molecular system in which it is exceedingly difficult to control absolutely the precursor mixtures and concentrations.

It is the purpose of this comment to point out that by properly equipping MO-CVD systems with suitable optical diagnostics, it is possible to have very specific controls on reactants and, further, that such diagnostics allow one to see and follow reactant intermediates evolved during the deposition process. For example, consider the growth of HgTe from Hg-atom vapor and gaseous dimethyl tellurium (DmTe). These reagents can be monitored by installing optical ports in the gas lines or CVD chamber and using tunable laser probes.

For example, Hg atom concentration can be measured by using laser induced fluorescence on the Hg resonant line at 254 nm. This UV wavelength is readily available from a frequency doubled dye laser. The DMTe concentration can be detected in the UV using a fixed or tunable UV laser in conjunction with a straight absorption measurement. In addition, it is possible to use an infrared diode laser to detect DMDC via a measurement of the vibrational lines at $3\mu\text{m}$.

Recently V. Donnelly and R. Karlicek at AT&T Bell Labs. have used such an array of laser probes to diagnose the growth of epitaxial indium phosphide in a vapor-phase system. An effort should be made to encourage the set up of such fully diagnosed systems.

2) In MO-CVD systems, metal alkyls, such as dimethyl tellurium or dimethyl cadmium; are common precursor molecules. Despite the importance of understanding the precursor molecular chemistry to the growth of high quality epitaxial films, there is a surprisingly small body of knowledge on the structure, properties, spectroscopy, or chemical purities of these materials. For example, it is very difficult to locate a tabulation of the vapor pressures of metal alkyls. In addition, the spectroscopy of these materials in the infrared and ultraviolet is in many cases unknown - even though such data are useful for quantitative analysis of the structure and purity of the molecular source.

An even more serious problem is the questionable purity of metalalkyl molecules. When a bottle is purchased from a commercial vendor, the purity of the contents are only stated in terms of the metal atom purity. As a result, large and varying amounts of hydrocarbons often appear in a freshly delivered bottle. Since these impurities have very different chemical properties than the metal alkyl precursors their behavior in the CVD chamber is different and unexpected. This stray chemistry may not strongly effect the growth rate of the semiconductor, however, it could well lead to carbon contamination and defects in the CVD material.

A final point, is that the available stock of organometallic gases for microelectronics seem largely to have been generated as a result of an empirical experimentation. For many applications particularly for low temperature growth or complex alloys a more systematic search for useful chemicals should be undertaken. This search should involve the collaboration of an active organic chemist and an experimentalist growing compound semiconductors.

SELF-ASSEMBLING ORGANIC MONOLAYER FILMS

George Whitesides

Appropriate organic materials (fatty acid derivatives, others) spontaneously form monolayer films at interfaces between hydrocarbon solutions and solids (silica, glass, alumina, gold, platinum, other metals). It is now qualitatively clear that:

- 1) These monolayers are highly ordered.
- 2) They can be formed from many different molecular components.
- 3) They can, in appropriate systems, be stable (they do not volatilize in high vacuum at room temperature).

Monolayer films of these types have a variety of potentially useful applications.

- 1) Variable width, high dielectric constant films for electronics use.
- 2) Colloid stabilizing agents for ceramic processing or dispersion of magnetic pigments (high storage density magnetic media, stealth).
- 3) Films capable of changing index of refraction or reflectivity in integrated optical devices.
- 4) Adhesion promoters in semiconductors packaging.
- 5) Barrier films for corrosion inhibition.
- 6) Substrates for attached tissue cultures.
- 7) X-ray mirrors.

All of these applications are presently speculative (although uncontrolled or non-optimized examples exist for all of them). To develop this technology, we need to deal with the broad, fundamental issues of synthesis/preparation, characterization, and structure-property relations.

Immediate objectives for our program are to answer these questions:

- 1) How wide a range of organic/organometallic components can be incorporated into spontaneously self-assembling monolayers?
- 2) How are these systems organized? Are they two-dimensional crystals, or two-dimensional glasses or liquids?
- 3) What are their physical properties as materials? Will they act as thin-film insulators? As barrier films for corrosion inhibitors? How do they modify index of refraction at interfaces? Will they act as "surfactants" on metal and metal oxide surfaces?
- 4) Can the individual components be synthesized to provide high temperature stability and/or chemical stability to these structures? Can one make them polymerizable, or form them in ways in which they interact strongly in the two-dimensional plane?
- 5) What are the best ways of forming multilayers, and monolayers containing more than one component? What are the structures of these systems?
- 6) What synthetic chemistry can be carried out on functional groups exposed on the outer surfaces? How does location of functional groups on surfaces influence their reactivity.

INTEGRATION OF SOLID STATE ELECTRONICS AND CHEMICAL AND BIOLOGICAL SYSTEMS

G.M. Whitesides and M.S. Wrighton

INTRODUCTION

This report stems from a two-day workshop held at the Materials Research Council on July 16, 17, 1984. The program, speakers, and the attendees are given in Appendices A,B, and C, respectively. The program was organized with the recognition that DARPA's interest in electronic sciences and materials sciences is evolving to include an important role for chemical and biological sciences. Though the field of "biotechnology" is presently receiving much attention from biologists and biochemists, there are areas of potential application in the military that are not completely well-defined and are not receiving the conscious attention being directed to health-oriented applications, for example. Part of the rationale for the lack of interest in military application from the biologists and biochemists rests in a lack of understanding of military problems. A lack of fundamental information transfer between scientists in different disciplines also appears to exist concerning issues such as what present electronic computers can do and what might be possible with biological systems. The purposes of the workshop were to bring together a group of people with educational backgrounds and research contributions in physics, electronics, chemistry, materials science, and biology to (1) discuss on-going and proposed research relating to interfacing chemical and biological systems with electronic devices and systems; (2) identify unique materials properties of natural or "engineered" biological substances; (3) learn about generic problems and opportunities for cross-cutting fundamental contributions

leading to applications of advanced bio-chemical technology; and (4) highlight those areas where DARPA could play a unique role in developing solutions to generic problems in advanced bio-chemical technology.

The term "advanced bio-chemical technology" refers to technology based on biology, biochemistry, and chemistry and should not be taken to refer exclusively to the more narrow area of "genetic engineering" or recombinant DNA technology. Rather, this term should be construed to include technology derived from the bulk or surface properties of natural or engineered biological materials or from the integration of chemical and biological materials with conventional solid state systems to form new kinds of devices such as ultraspecific, ultrasensitive sensors. Study of biological systems may also "inspire" new kinds of synthetic systems for achieving the same function under controlled conditions.

SUMMARY OF MEETING

The meeting consisted of an introductory overview of DARPA's programmatic interests followed by thirteen individual presentations and concluded with an overview and discussion session. The highlights of material presented at the meeting are summarized in the sections below.

Interfacing Solid State Electronics With Chemical Systems. There were several presentations that dealt exclusively or partially with the specific problem of a direct interface of electronic devices with chemical and biological systems for the purpose of achieving a sensor. Janata opened the meeting with a description of work on chemically sensitive field effect transistors, Chem FET's, and underscored several important issues of generic importance including (1) the genuine need to develop ultrasensitive,

ultraspecific sensors for aqueous systems using electronics that abhor H_2O and (2) that interfacing solid state electronics with chemical and biological systems involves the interface between electronic and ionic conductors. Hughes illustrated one military area where Chem FET's or chemically sensitive Schottky barriers could be useful owing to their small size, sensitivity, and low power consumption, namely detection of gases (H_2 , O_2 , NH_3 , etc.) in stockpiled nuclear weapons. He raised a generic issue in analytical chemistry concerning specificity. An overview of various sensor issues was provided by Zemel and he emphasized the need to be concerned as well with response. The distinction between monolithic and hybrid sensing devices was made and he expressed the view that the hybrid devices are more likely to be practical.

Other presentations included aspects of relevance to sensors, and analytical applications of bio-chemical systems were a recurring theme both in presentations and discussions. Lamola emphasized the importance of examining biological systems from the standpoint of inspiring new kinds of devices. During the summary, for example, he described the electrical interfacing of a small living system to give an electrical signal in response to a chemical stimulus after the living system "learned" the procedure. At a more molecular level, Montal showed that single molecule response could be detected when a small bilayer membrane containing one acetylcholine receptor ($1\mu m$ diameter) served as an ion gate between two compartments of an electrochemical cell. The opening of the "gate" by binding a single molecule to the receptor was shown to result in a flow of Na^+ ions of the order of $\sim 10^7$ ions/s. The frequency of channel opening was shown to depend on the concentration of the species to be bound and the potential across the

membrane. Erhan noted the possible applications of biological materials as piezoelectric and pyroelectric detectors. Wrighton emphasized the need to do fundamental work on surface chemistry of electronic devices to interface well with biological molecules while avoiding surface fouling. He indicated approaches to "building-up" sensor functions from molecules by assembling molecules in ways that give amplification of a chemical signal such as pH variation. In his general overview Whitesides noted the importance of exploiting the amplifications associated with biological systems, e.g. enzyme catalysis. Further, there should be a broader consideration of methods for detecting, antigen-antibody binding. Optical, acoustic, and magnetic methods should be considered in addition to electrochemical methods.

Biological and Chemical Materials. Several presentations focused on pure materials, biological and synthetic, that could be useful as components, structural and active, in a variety of systems. The biological magnetic materials discussed by Blakemore have no immediate applications, but understanding Nature's compass may lead to ways of synthesizing magnetic materials and exploiting cooperative phenomena. Uzgiris illustrated elegantly the possibility of preparing large, 2-D crystals of proteins to uncover important structural information about large proteins that may not be amenable to characterization by x-ray crystallography. Montal, similarly, illustrated that structures based on biological membranes can be useful in understanding properties of membrane-bound proteins. Proteins were the theme of Erhan's presentation, as well, with the view that polypeptides could be synthesized to realize chemicals with desired properties. Presentations by Parshall, Arrhenius, Metzger, and Wrighton focused on non-biological materials. Parshall outlined some views of future opportunities for

chemistry in materials. Two areas, ceramics and optical materials, will comprise a substantial research effort at DuPont. This emphasis represents a significant departure from DuPont's traditional interests. As such this serves as one sign of the change afoot in the chemical industry and the perception that new commercial opportunities lie 5-10 years ahead in advanced materials through chemistry. Arrhenius outlined some prospects for exploiting naturally occurring superlattices by making inclusion compounds to synthesize novel hybrid materials. Metzger outlined the theory underlying a molecule-sized rectifier. The synthesis and characterization of candidate molecules is underway, the general assembly consisting of a donor-connector-acceptor. In his presentation Wrighton also emphasized a role for molecule-based materials, especially redox polymers and electronically conducting polymers.

Biological Computers. The aims of the workshop did not include evaluation of the prospects for so-called biological computers. However, the participants were of the general opinion that biochips would not replace Si/SiO₂ electronics in the foreseeable future. Both Lamola and Yates firmly indicated that biochips are not a technology now. Lamola carefully outlined major fundamental obstacles (speed of charge transport, realistic size) to doing computing with organic or biological materials as we now understand them, though he expressed the view that there are definite things to learn from complex biological systems that might be of relevance to electronic systems. Yates emphasized a need to understand the networking of biological systems such as the brain to achieve more efficient networking for computers based on solid state electronics.

Biological Systems and New Devices. Some biological systems have no man-made analogue and achieve highly desired functions. For example, Lamola pointed out the natural photosynthetic apparatus as a means for converting sunlight to useful chemical energy. Whitesides noted the chemical energy system associate with oxidative phosphorylation. The ability to achieve pattern recognition within short periods of time with individual switching elements having a time response of ~1ms indicates the considerable power of biological systems as highlighted by Yates and others. Metzger presented approaches to achieving unidirectional electron transfer with small molecule (~25Å) assemblies. In his presentation Wrighton outlined approaches to using macromolecular (~10,000Å) assemblies to achieve devices that can amplify electrical or chemical signals, pass current in only one direction, and emit light upon input of electrical signals.

PRINCIPAL ISSUES IN ADVANCED BIO-CHEMICAL TECHNOLOGY

The workshop and associated informal discussions among participants and MRC members have led to the identification of a number of key scientific, engineering, and technological issues in the area of advanced bio-chemical technology. These issues fell into four broad categories: materials, manufacturing, materials structures, and devices. Aspects of each of these areas are highlighted in the sections that follow.

New Biological Materials. A revolution has occurred in molecular biology in the last ten years. One important application of the practical technology derived from this scientific activity has been a dramatic increase in the accessibility of biopolymers -- proteins, polysaccharides, nucleic acids -- a group of substances which had previously been largely

inaccessible. One interest in biotechnology from the vantage of materials science stems from the possibility that these biopolymers may serve as components of useful systems, adhesives, surfactants, films, fibers, lubricants; molecular sensors for new analytical devices; rheology control agents for water. The major focus of research in biotechnology has been, to the present, in health-related areas, and relatively little work on other applications. Given the existence of this fundamentally new technology for production of complex and previously inaccessible substances, the central questions concern utility:

- Are there applications in which materials derived from biopolymers have properties superior to those produced by conventional chemical methods?

- Are there circumstances in which the types of processes employed in biotechnology are preferable to those of conventional chemicals and materials processes?

- How practical and economical are large-scale biotechnological processes?

It should also be realized that biological materials can be used in the "as is" state, e.g., wood for construction; after isolation and purification, e.g. natural fragrances, flavors; or after harvesting and post-chemical treatment. Thus, post-treatment of naturally occurring biological materials further elaborates the possibilities with respect to available materials properties. For example, treatment of cotton (a useful fiber material) with nitric acid to convert it to nitrocellulose (gun cotton) remarkably alters its properties. While the focus of this report is on materials derived from biology it should be emphasized that conventional chemical methods will be

applied to the preparation of new materials. In particular, it is noteworthy that DuPont, and other large chemical companies, are turning their research resources and expertise to new commercially viable routes to ceramics, nonlinear optical materials, organometallic molecules for CVD processes, new resists, and other "speciality" chemicals and materials. The point is that biological materials do have interesting properties, but there may be traditional methodologies that work equally well and are more commercially viable. Thus, conventional synthetic chemistry represents a baseline against which new, biologically derived materials should be judged.

Each of the major classes of biologically-derived substances of interest in materials science has a particular set of central technical issues, and each is discussed in the following discussion in turn.

A. Proteins. Biotechnology, especially recombinant DNA (rDNA) and hydridoma technology, has made it practical for the first time to consider proteins for economically practical use in materials science, and to "design" (that is, to specify the molecular composition) of proteins with great flexibility. The most important technical issue is now that of the relation between protein structure and protein properties: What protein structures provide useful properties?

At present it is impractical to make any but the very simplest connections between protein structure and molecular properties such as folding and shape; it is more difficult yet to connect protein structure and a materials application. A major technical problem thus centers on what is a problem in the basic science of proteins, and of protein-derived materials: What amino acid sequence gives a protein particular properties (shape, shape stability, surface activity, adhesive properties). Note that the problem of

relating atomic - or molecular - level structure to macroscopic physical or materials properties is pervasive throughout materials science, especially in polymer chemistry and metallurgy. It may be particularly useful to address this problem in the context of proteins, since rDNA technology has provided very wide variation in the structures of these materials, but the advantage conferred by this ability to vary structure widely must be balanced against certain intrusive disadvantages of proteins in materials applications -- especially a general tendency to be unstable at high temperature.

At least three approaches exist for developing structure/property relationships for proteins:

i) Examine structure/property relationships in naturally-occurring proteins. A number of proteins exist in nature which have interesting materials properties; for example, spider silk has high tensile strength; barnacle cement is an excellent adhesive which bonds under water; collagen forms biocompatible fibers and films. By studying these systems, or by the more empirical approach of examining materials obtained from other, readily available proteins, it may be possible to observe generalizable structural features that can be correlated with useful material properties.

ii) Examine structure/property relationships in synthetic polypeptides. A current belief in protein chemistry is that many of the important properties of proteins are associated with polypeptide domains -- small regions of protein (20-50 amino acids) -- having local structural integrity. Work focused on the design and synthesis of domains would, if successful in providing the ability to design domain - forming sequences, form

a very important foundation for rational structure/property relationships in proteins and protein assemblies.

iii) Calculate protein structure/property relations. Large computers now make it possible to begin to calculate equilibrium conformations of proteins. These problems are technically very lengthy (a representative protein contains ~2000 atoms, excluding solvent) and requires both access to large computers and disquieting simplifying approximations (neglect of entropic terms). These calculations are, nonetheless, providing important fundamental understanding of protein structure/conformation relationships. Progress in this area of calculation is limited both by a shortage of thermodynamic data to build into the computer models, and by limited access by research groups working in the area to large computers.

An important subclass of proteins whose utilization poses problems unrelated to those involving protein-based materials are monoclonal antibodies (MAb). The hybridoma technology used in making these molecules offer unique capacity to design protein complexing agents which show very high specificity in their molecular recognition and binding properties. This specificity is the basis for important new analytical methods. Fundamental detail concerning the biological steps leading to these molecules is still missing, and techniques which produce new hybridomas, especially hybridomas yielding antibodies with high affinity constants ($K > 10^{12} \text{M}^{-1}$) or antibodies against scarce or weakly-antigenic substances, are not as rapid or efficient as would be desired. Work directed toward unraveling the details of the initial stages of the immune response, and toward hybridoma production and selection would be very useful in developing new MAb's for

analytical applications. Some work directed toward these problems is in progress in universities and biotechnology companies, but this work is addressing only parts of a very complex problem.

B. Polysaccharides. Polysaccharides already have a range of uses in a commercial sense, primarily in the area of rheology control for aqueous solutions. Biotechnology has also made these substances more readily available, primarily by improvements in techniques for isolating and growing the microorganisms producing them. One fundamental question posed in this area is again that of structure/property relationships: What polysaccharide structures can be associated with useful properties?

Because the ability to control the biosynthesis of polysaccharides is presently much more primitive than that for proteins, two quite different types of technical problems limit the ability to develop new, useful, polysaccharides:

i) The "classical" methods for developing fermentation products -- microbial strain identification, strain optimization, and growth -- are very inefficient for polysaccharides useful in typical materials applications, especially if the utility does not emerge until after post-isolation chemical modification has been carried out. The development of new screening techniques to identify microbial strains producing useful products would greatly accelerate the rate of progress in this area.

ii) The basic biochemistry and molecular biology required to specify the biosynthesis of polysaccharides having non-natural sequences is not available. There is no equivalent to recombinant DNA technology for polysaccharides. The practicality of transferring the complex enzyme systems of polysaccharide biosynthesis from one organism to another, the

use of multiple enzymes to make polysaccharides, and the ability to control excretion all remain to be demonstrated and developed. Only when this preliminary work has been done will it be possible to make polysaccharides with some of the flexibility now possible for proteins.

C. Nucleic Acids. Nucleic acids (DNA and RNA) themselves have little or no direct utility as components of materials systems, but they (especially, using current technology, DNA) are fundamental to advanced biotechnology. DNA sequences coding for amino acid sequences interesting in biotechnology have not been developed, and both their synthesis and their manipulation in vivo may require the development of new techniques. For example, a DNA sequence leading to a polypeptide sequence having a very high concentration of positively charged amino acids (e.g., poly-L-lysine, a candidate for adhesives applications) seems to be difficult to express in vivo, perhaps because this type of polymer complexes with and inactivates negatively charged biopolymers. The amount of effort which has been devoted to the synthesis and manipulation of DNA coding for entirely non-natural proteins has been very small, and it would be surprising if unexpected phenomena did not arise in initial experiments in this area. Exploratory research directed toward the synthesis of model proteins representative of those of potential interest in materials science would be useful in guiding future design in the area, and in assessing the feasibility of materials production by biotechnology.

D. Lipids. Biology offers routes to certain other useful classes of materials. Lipids, for example, may find use in modifying water surface tension ("seabreaker"), in stabilizing colloids in ceramic processing, in biosources, and as lubricants. Examination of the interfacial properties of

biologically produced surfactants in seawater, and the development of thermophilic, halophilic, and other anaerobic organisms (as well as plant varieties) as sources of lipids and fatty acids will produce useful new substances.

Synthetic/Manufacturing Methodology for Biomaterials.

Biotechnologies have a common base in biology: living cells or catalysts derived from living systems (enzymes) are used to effect chemical transformations. One useful characteristic of biotechnology is that it provides a relatively simple production technology leading in one or few steps from readily available, structurally simple starting materials to complex products. Any program to produce a new biomaterial can be divided into three stages:

- i) Obtaining or developing a suitable production organism or enzymatic catalyst.
- ii) Developing a practical process
- iii) Isolating the product
- iv) Fabrication of the final system

The fourth stage -- fabrication -- occurs in all materials science, and is often the most critical stage in determining the properties of the material. There may be opportunities to develop "self-assembling" systems based on biologically-derived or biologically-inspired systems.

A. Protein Products. Three groups of protein production problems are now apparent, based on cost of products.

- i) High-value proteins, especially MAb's. The production cost of MAb's is now approximately \$5000/g by several well-established technologies. This cost may be expected to decrease by a factor of 10 in the

next five years using developments of existing technology. New technologies are also being pursued in many laboratories. The major unknown cost is now the initial, one-time cost of developing a suitable hybridoma: the cost of this stage can vary from \$10,000 to >\$0.5M, depending on circumstances; luck in screening, efficiency of the antigen, and other factors. The major opportunity in this area for the DOD would be to stimulate research directed toward the problems of generating the producing cell line: that is, to develop new techniques for hybridoma production, or for rapid, automated identification and selection of hybridomas or mature B lymphocytes. One of the problems worthwhile pursuing is investigation of the basic cell biochemistry leading to production of mature B lymphocytes: Antigen presentation; interaction of the antigen presenting cell with the helper T cell and the immature B cell; maturation; switching. Basic science in this area will lead to greater efficiency in antibody production. A second is the development of techniques appropriate to the particular problems of the DOD, especially identification of toxic substances.

ii) Protein Products for use as Specialty Chemicals (in adhesives, surfactants, fibers and films). The cost of these materials must, presumably, be less than ~\$100/pound. Few precedents exist in this area, but production of materials with unusual properties (adhesive, viscosity enhancing, surfactant) clearly pose major problems in reactor design and operation. These problems have been addressed only incompletely in fermentations yielding viscosity-enhancing polysaccharides (xanthan gum) and in managing foam formation in fermenters.

iii) Small-volume reactors. Biotechnology may afford the opportunity to make biopolymers in the field from locally available starting

materials. For example, shipboard production of drag reducing agents or lipid surfactants is possible. Such applications clearly place a premium on compact size and ease of operation of the biochemical reactors. This type of military application has no civilian counterpart, and the problems of reactor design relevant to this type of operation are unknown. One broad, generic problem concerns the relative attractiveness of aerobic and anaerobic fermentations for this type of application. Aerobic fermentations are relatively easy to run, but suffer from limitations to rate and cell density imposed, often, by difficulties in introducing oxygen into solution sufficiently rapidly to overcome mass transport limitations. Rapid gas introduction may lead to problems in foaming; hyperbaric operation is expensive and may result in oxygen toxicity. Anaerobic organisms can grow to much higher cell densities than aerobes and present fewer problems with foaming. The organisms are, however, more difficult to work with. A systematic evaluation of the relative characteristics of compact aerobic and anaerobic bioreactors would guide future work in this area.

B. Polysaccharides. The problems in production of polysaccharides are similar to those outlined for proteins, and fall in the categories of general problems in biochemical engineering (especially process control and operation, and separations) and specialized problems in design and operations of compact reactors.

C. Fabrication. The fabrication of materials from biopolymers is an untouched area. The simplest applications will be in areas requiring little or no fabrication - drag reduction by polysaccharides, wave suppression with surfactants, or lubrication. The second level of complexity is presented by analytical applications - how should biopolymer molecules capable of highly

specific recognition be interfaced with optical or electronic devices? The third level of difficulty is involved in the use of biopolymers or biopolymer derivatives as functional specialty chemicals - adhesives, corrosion inhibitors, antifouling agents.

Structure of Materials. Biotechnology now provides methods for making previously inaccessible classes of molecules, especially proteins, polysaccharides, and nucleic acids. The utility of this technology in health-related areas (including food and agriculture) is evident, and utility of particular biologically-based candidates for medicinal agents can be evaluated straightforwardly. The utility of this technology in materials science or specialty chemicals is less immediately obvious. What useful materials and chemicals are best obtained by biological processes?

The interest in biotechnology from the vantage of materials science is that it provides a very large new class of polymeric substances for investigation. Many indirect arguments suggest that certain of these substances will be useful. For example, proteins are polyamides, and petroleum-derived polyamides (nylons) are exceptionally useful structural and fiber materials. Only a few polysaccharides are readily available, and of these several (xanthan, carrageenan, hyaluronic acid, agar) have unique rheological properties in water solutions. Nature provides further examples of materials - like uses of biopolymers: spider silk as a fiber; collagen for tendons and connective tissue; lens proteins in the eye for optical lenses; barnacle cement for adhesion; abalone shell and bone as protein - inorganic structural composites; lipid bilayers as thin film insulators. Intuition suggests that biopolymers will be useful in materials science, but the best directions to pursue to develop new materials are not obvious. How should

this promising but unproven field proceed? What hinders its development?

One major problem is the virtually complete absence of a sound scientific basis for predicting the materials properties of new biopolymers from their molecular structure. Biotechnology provides the opportunity to make a very large number of new polymers; most of a randomly chosen sample will be useless. For efficient development, there must be some way of choosing promising target structures. A program designed to understand relationships between amino acid or sugar sequences and secondary and tertiary structure (the shapes of the molecules) would represent a starting point in understanding these relationships. Research in this activity has been conducted for many years, but recent advances in polypeptide and polysaccharide synthesis, coupled with new theoretical and computational approaches, provide new opportunities.

A second problem is that the interesting naturally occurring material structures (silk, membranes, bone, teeth, tendon, barnacle cement, insect shell, etc.) are themselves poorly understood, and thus neither permit duplication nor stimulate modeling. An effort to understand structures occurring in nature which have unusual materials properties would suggest high-strength fibers and composites, adhesives, engineering polymers, lenses, and insulators, and suggest strategies for using biopolymers in materials science.

The natural world also includes inorganic materials having interesting structural properties. Such materials include clays and minerals, which in combination with organic and/or biological materials could offer a new class of solids having unique properties. Zeolites are already known as "shape selective" catalysts that operate at high

temperatures. Also, conducting metal disulfides can be intercalated and used as electrical energy storage media. Finally, there are fundamental issues relating to the origin of life that stimulate interest in clays and clay chemistry. At this point, the hybrid materials to be formed from highly structured, natural inorganic solids and organic and/or biological materials remain as an unexplored, potentially fruitful area of fundamental inquiry.

New Devices. Semiconductor technology is highly successful. Can useful, non-computing devices (e.g. sensors) be developed based on new biological, or chemical concepts or components coupled with semiconductor physics? Does biology or biochemistry have contributions to make to semiconductor technology? Does biology or chemistry offer alternatives to it? We address these questions in order of practical priorities.

A. Analytical Devices and Sensors. It is clear that a major opportunity exists to develop new types of sensors and analytical devices based on new chemical and biological techniques. Biology offers several classes of molecules which have high capacity for specific recognition. Of these, the most immediately useful are monoclonal antibodies (MAb). Analytical procedures based on MAb's are, of course, already highly developed in clinical analysis. The particular applications of the DDD -- ultratrace analysis, simple, reliable field use, continuous monitoring, analysis of reactive and toxic substances, high-reliability testing -- will require new technologies.

Three generic problems require solution: First, new technologies are required to generate MAb's (or other biorecognition substances) more efficiently, and with higher binding constant toward antigens. High-sensitivity analysis requires tight binding. Second, new or improved methods are

required to interface the MAb or other biologically derived recognition system with electronic systems. Electrochemical approaches to interfacing biological and electronic systems are progressing smoothly and should be continued. These systems are, however, not easily applied to MAb-based systems, nor probably applicable to many problems in ultratrace analysis. Optical methods seem particularly promising, since they have high sensitivity, are applicable to remote monitoring, and may be capable of capitalizing on new technologies such as fiber optics or optical computing. Other techniques -- thermal, magnetic, acoustic, -- may also be worth developing.

Third, inert, non-interfering systems must be developed to package the analytical components. Ultratrace analysis requires that the small quantities of the substance of interest reach the detector (whatever its nature), rather than absorbing on the non-detecting parts, of the apparatus or collection device. This type of supporting technology is critical to reliability in ultratrace analytical procedures. For other types of sensors, chemical approaches (electrochemical and other) hold great promise. Techniques for miniaturization of electrode assemblies, and for coating them with electroactive polymer films, offer the prospect for both new, small sensors, and for high selectivity in certain types of sensing processes. One problem which may be troublesome in the development of small "hybrid" systems -- those combining semiconductor devices and electrochemical components -- has to do with the environment for these systems. The electrochemical systems require water (or some ionically conductive medium) for operation. Semiconductor devices are damaged by such media. These two must be separated physically, or the semiconductor components must be isolated from the water. (This requirement with its resulting

complexities is one argument for optical rather than electrical probing of the sensor element.)

There is a clear and important connection between work on microsensors for chemical and biological systems and solid-state electronics. Basically, the microsensor program presents an ideal opportunity not only to build devices which are intrinsically interesting but also to test and experiment with devices containing entirely new material systems. Good examples of this point are transistors with organic passivating films and gates. Some of these unusual device structures will undoubtedly lead to novel devices for electronic applications.

B. Can chemistry or biology contribute to or replace high-speed digital computers? Chemistry will continue to contribute to semiconductor device technology, and the prospects for development of new etching and CVD processes seem excellent. At the moment, there are few obvious places where biologically-derived materials would seem useful in semiconductor device technology, although techniques for forming monolayer films containing fatty acids, proteins, and other biological components offers clear promise at the research level. It is evident that electrochemical, biochemical, and biological devices will not replace semiconductor devices for the tasks for which the latter are optimized. In particular, the "biochip" -- the hypothesized assembly of biologically-derived or biologically inspired molecules constructed to mimic semiconductor-like electrical functions -- probably cannot be made, and certainly would not compete with a programmable computer in any event. The subject of biologically-based computers has been the subject of considerable speculation in the popular literature and in venture capital circles, but much of this speculation had

been based on unproven and probably unworkable concepts, and the enthusiasm for the area stems from its combination of two "hot" topics -- computers and biotechnology -- rather than from its probability of producing useful new technology. It is important to proceed with real caution in this area. If research is to be conducted on any biological or chemical approaches to electrical signal processing (and such research seems very attractive in such areas as thin films and electroactive organic materials), it should be considered basic and exploratory, and supported at an appropriate level until concepts have been proved. Nothing in this area presently justifies a large scale development program.

C. Are there other ways in which biology and chemistry might benefit information processing? At the conceptual and research level, the answer to this question is clearly yes. Information processing in biological systems proceeds by strategies which seem to be quite different than those used in semiconductor devices. Study of biological strategies for forming networks, for storing and retrieving information will unquestionably be stimulating, and may contribute to the development of solutions for certain types of specialized analog problems (pattern recognition, training, speech recognition and translation) which are difficult with current programmable digital computers. In addition, examination of the molecular-level components of biological information processing systems (ion channels, receptors, polarized lipid membranes) will contribute to research in the exploratory area of "molecular electronic". The ion channel in a biological membrane is, for example, an authentic single-molecule ion switch, and biological systems display a rich variety of successful strategies for transmitting information based on ions and chemicals, rather than on electrons. Understanding these

strategies should be intellectually stimulating for those concerned with computing strategies and with molecular electronics, and might contribute directly to the broad problem of interfacing biological and electronic systems ranging from biologically functionalized sensors to neural prothesis.

Molecular electronics -- the development of new chemical systems having useful electrical properties -- is still in its infancy. It is an area of real interest, but it is still far from practical devices. Some of the research in this area is, however, based on ideas which are conceptionally sound and interesting (organic rectifiers based on ordered thin films). Other materials which fall peripherally in this area (organic materials for frequency doubling, electrooptical materials) may well be the best available. In any event focusing the synthetic talent available in organic and organo-metallic chemistry on problems in preparation of new electrically/optically active materials can only benefit the makers of electronic devices.

Another very important aspect of this work is that it presents an opportunity for learning to fabricate device microstructure of organic films. Organic microfabrication is increasingly becoming an issue in micro-electronics manufacturing. For example, ceramic chip carriers require that interlayers be made of low dielectric polymers. New research in fabrication technology for organics such as deposition and dry and wet etching, which will be developed on the microsensors program, is of direct concern for future electronics research.

A particularly important consequence of the thin organic and biological films which could be developed by a research effort in biochemical technology is that they may form useful materials for electronics microfabrication. The specific qualities of these films, such

as microstructure adhesion, and etching properties determine specifically whether a particular microfabrication sequence can be performed. Biological and self-organizing films offer a unique opportunity for controlling and adjusting these film properties. For example, it is possible, in principle, to tailor the adhesion of film molecules to certain surfaces and not to others or to adjust the microstructure so that etching or anisotropy are built into the material. The two-dimensional crystalline films may offer a structure which allows sharp patterning even on angstrom scales.

OPPORTUNITIES FOR DARPA

There are numerous fundamental areas where DARPA can make a crucial or unique contribution to fostering the development of biochemical technology of relevance to DOD missions. But it is also clear that "biotechnology" is supported heavily in the private sector and by the government for health and medical applications. These areas will undoubtedly generate a science base and some applications of interest to the DOD, but an advanced bio-chemical technology program at DARPA does not seem warranted on the basis of health and medicine applications. A DARPA program is justifiable on the basis of a likely contribution to new technology based on (1) unique properties of material that can be found in nature or of materials that can be obtained by genetic engineering, (2) receptor properties of biological materials for use in analytical devices that are ultrasensitive and ultraspecific, (3) utilization of biological systems directly for portable production of materials of military significance, and (4) expertise and capability derived from knowing how biological systems

achieve their function such as energy conversion and pattern recognition that can bring about the development of new devices for achieving such functions in man-made systems. A program leading to applications can be expected to show proof-of-concept laboratory demonstration in a part time period as short as two years, e.g., analytical biopolymers for drag reduction, but in general, the time frame for applications will be five to ten years and longer in some areas.

The DARPA opportunities can be broadly classed into three areas: generic science, material devices, and engineering. Some of the key areas that can be identified now are indicated in the sections that follow.

Generic Science. In the biological materials area the science base required to predict the structures of new biopolymers intended for specific application is inadequate. Indeed, the science base is inadequate to relate structure and function of known biological materials. Research on structure-property relationships should be both experimental and theoretical with the aim being to rationalize and predict the relationships between molecular structures and macroscopic materials properties of structurally well-defined proteins and polysaccharides, and of short molecular fragments corresponding to structural domains of these substances. Structure-property relationships have proven crucial to the development of small molecule chemistry and it is clear that similar information is needed for large, complex, biological molecules.

A second problem of generic importance is one of interfacing biological systems with the world of solid state electronics. Analytical devices, vide infra, represent a genuine area of opportunity, but the problem of interfacing electronic conductors with ionic conductors is difficult and the

general notion of exposing electronic devices to aqueous media is an obstacle of significance. The incompatibility of synthetic surfaces with biological systems is a well-known difficulty that can, in principle, be solved by clever surface modification schemes.

In the "biotechnology" area, the techniques for microbial strain selection and manufacturing monoclonal antibodies and the like are time-consuming, labor intensive, and generally inefficient. What is needed, basically speaking, are ways for automated selection of individual cells having desirable properties from a mixture of cells. Development of analytical procedures for optical scanning, recognition, and sorting should be encouraged.

Intellectual excitement in biology stems, in part, from great challenges associated with understanding how complex systems work. Understanding the "networking" in biological systems is crucial to learning how complex pattern recognition is accomplished rapidly when individual agents give a response on the millisecond timescale. Neurobiology of the brain and central nervous system will be especially important areas of research. These efforts should contribute to development of analog computers.

Materials. Biological materials having unique properties and synthetic speciality chemicals and materials represent important opportunities for DARPA. Many of these opportunities have been identified above, but the following list of possibilities should serve to illustrate realistic application areas and stimulate additional thought:

- Surfactants
- Adhesives
- Lubricants
- Corrosion Control Agents
- Enzyme Catalysts
- Insulating Thin Films
- Pyroelectric Materials
- Piezoelectric Materials
- Organometallics for CVD
- Non-Linear Optical Materials

In the biological materials area genetic engineering certainly provides an unlimited number of possible new materials, but the development of practical biochemical processes for production of adhesives, surfactants, and rheology control agents, for example, will require solutions of new problems including promotion of cellular production of high concentrations of unnatural polypeptides. How, for example, will one collect an adhesive from the environment in which it would be expected to function?

Unusual organisms offer the prospect of both new material and procedures for making them. Microorganisms living in high-temperature, high-salt, or high-pressure environments offer a rich source of useful new enzymes and biological systems. These organisms are also important in microbial fuel contamination, in marine corrosion, and in microbial ore processing. An exploratory program directed toward the development of culture techniques for these organisms, and toward a survey of their metabolism and enzymology would indicate the extent to which this area should be developed as a source of biological catalysts or materials, or as

components of biological systems (e.g., for disposal of hazardous wastes and decontamination of toxic substances; for suppressing or promoting corrosion, biodegradation and fouling).

New Devices. Materials having unusual properties can be useful in fabricating new devices. The possibilities for analytical devices using biological materials are especially promising. Such devices based on biorecognition using monoclonal antibodies will require the development of techniques for preparing antibodies having very large antigen-antibody binding constants. Detecting the antigen-antibody complex electrochemically, optically, magnetically, acoustically and by other means should be investigated. Exploiting the amplifying power of biosystems (e.g., enzyme catalysis) should be encouraged. Analytical applications of bio-chemical technology can be expected to be developed within five years.

New electronic devices other than analytical from biological and synthetic materials can be envisioned. The ion channel based on a single molecule in a bilayer membrane represents a real molecular switch, albeit based on a large molecule. The switch can be opened or closed in response to chemical and electrical signals. Whether this sort of research directed toward polymer-based and molecule-based devices will pay off in practical terms remains to be seen. For now, these should be regarded as exploratory efforts that will lead to understanding of how to synthesize aggregate systems to achieve functions starting from molecular building blocks. DARPA should not view this area as one leading to near term replacement of conventional semiconductor electronic devices. No large scale effort to develop so-called "biochips" or a "biological computer" is justified at this time.

Engineering. Process scale-up and control, and product separation and purification are problems which presently limit all of biotechnology. Work directed toward new sensors for process control and new separation techniques based on membranes and selective absorbents seems particularly promising. Work in bioengineering for the manufacture of speciality chemicals and materials is especially needed. In the military setting, there are special requirements that necessitate bioengineering effort. On board reactors to produce biopolymers to reduce the drag and noise of submarines seem possible, but the engineering effort will be one that breaks new ground in the field of bioengineering.

CONCLUSIONS

Devices and materials from advanced bio-chemical research are a certainty. There is an excellent possibility that some of the materials and devices will be unique, and it is realistic to expect that important practical applications will emerge. Microsensors for toxins, interfaced to solid state electronics, and capable of detecting ultratrace levels with desired specificity appear to represent realistic opportunities and work should lead to proof of concept in five years or less. Materials for drag and noise reduction of ships are viable possibilities, but will require significant developments in bioengineering. Numerous other possibilities exist for practical exploitation of the fields of biology and chemistry, ranging from the understanding necessary to developing new computer networking schemes to synthesizing materials for detection of single molecules.

DARPA is in a unique position to foster the development of bio-chemical technology for military missions. More than usual integration of

the disciplines of chemistry, biology, chemical engineering, physics and electrical engineering is required. It is safe to conclude that a discipline-based approach here will be far less successful than the interdisciplinary approach. The research is complex and requires efforts by groups having broad expertise and access to a wide range of facilities. That pay off is certain may be too optimistic a conclusion, but the conscious effort to achieve new materials and devices, coupled with the exploitation of results from the revolution in bio-chemical sciences of the past decade, provides a good level of assurance that substantial practical successes can be realized. DARPA should proceed with caution; "biochips" are not a likely outcome of even an excellent research effort. From the standpoint of the science, DARPA has the opportunity, though, to foster the creation of a new area of technology based on concepts from bio-chemical research. The field is rich with intellectual strength, enthusiasm, and promise. Industries are poised to commercialize new research. Areas of interest to DOD are not well-covered in existing research programs outside DOD. DARPA is encouraged to pursue an aggressive program in advanced bio-chemical technology and to monitor the state of the field, scientifically and technological, and to expand the effort as new intellectual and practical opportunities arise.

APPENDIX A

AGENDA

INTEGRATION OF SOLID STATE ELECTRONICS AND CHEMICAL AND BIOLOGICAL SYSTEMS WORKSHOP

JULY 16-17, 1984

Torrey Pines Elementary School, La Jolla, California

July 16

Introduction and Statement of Purposes

Dr. Ira Skurnick, DARPA/ESO

Dr. Mark S. Wrighton, MRC/M.I.T.

"Key Issues and Interfacing Chemical Systems with
Microelectronic Devices"

Dr. J. Janata, University of Utah

"Development of Chemical Microsensors"

Dr. R. C. Hughes, Sandia

"Chemical and Biological Sensors"

Dr. J. Zemel, University of Pennsylvania

"Applications of Biological Materials in Electronic Systems: A
Realistic View"

Dr. Angelo Lamola, AT&T Bell Labs

"Chemistry and Electronic Materials"

Dr. George Parshall, DuPont

"Biological Materials and Computers"

Dr. F. E. Yates, UCLA/Crump Institute

"Ion Channels and Receptors in Lipid Bilayers: Biological
Microsensors"

Dr. M. Montal, University of California, San Diego

July 17

"Magnetic Materials in Biological Systems"
Dr. R. Blakemore, University of New Hampshire

"Two-Dimensional Protein Crystals"
Dr. E. Uzgis, GE R&D Center

"Molecular Electronic Material"
Dr. G. Arrhenius and Dr. M. B. Maple, University of California, San Diego

"Adhesive, Bioelectric, and Pyroelectric Biological Materials"
Dr. S. Erhan, Albert Einstein Medical Center

"Towards Organic Rectifiers"
Dr. R. M. Metzger, University of Mississippi

"Chemical Based Microelectrode Devices"
Dr. M. S. Wrighton, M.I.T.

"Identification of Research Opportunities, Summary"
Dr. G. M. Whitesides, Harvard

APPENDIX B

SPEAKERS IN DARPA/MRC WORKSHOP

"INTEGRATION OF SOLID STATE ELECTRONICS CHEMICAL AND BIOLOGICAL SYSTEMS"

Professor Gustaf Arrhenius
Department of Oceanography
Scripps Institute of Oceanography
University of California, San Diego
La Jolla, California 92093
(619)452-2961
"Molecular Electronic Materials"

Professor Richard Blakemore
Department of Microbiology
University of New Hampshire
Durham, New Hampshire 03824
(603)862-2250
"Magnetic Materials in Biological Systems"

Dr. Semih Erhan
Albert Einstein Medical Center
York & Tabor Road
Philadelphia, Pennsylvania 19141
(215)456-7219
"Adhesive, Bioelectric and Pyroelectric Biological Materials"

Dr. Robert C. Hughes, Supervisor
Microsensor Division 1142
Sandia National Laboratories
Albuquerque, New Mexico 87185
(505)844-8172
"Development of Chemical Microsensors"

Professor Jiri Janata
Department of Bioengineering
University of Utah
Salt Lake City, Utah 84112
(801)581-3837
"Key Issues and Interfacing Chemical Systems with Microelectronic Devices"

Dr. Angelo Lamola
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey 07914
(201)582-2645
"Applications of Biological Materials in Electronic Systems: A Realistic View"

Professor Robert M. Metzger
Department of Chemistry
University of Mississippi
University, Mississippi 38677
(601)232-7301
"Towards Organic Rectifiers"

Professor Mauricio Montal
Department of Biology
University of California, San Diego
La Jolla, California 92093
(619)452-3665
"Ion Channels and Receptors in Lipid Bilayers: Biological Microsensors"

Dr. George Parshall
Director of Chemical Sciences
E. I. DuPont deNemours & Co., Inc.
Central Research and Development Experimental Station
Wilmington, Delaware 19898
(302)772-3277
"Chemistry and New Electronic Materials"

Dr. E. Uzgiris
General Electric Company Research & Development Center
Post Office Box 8
Schenectady, New York 12301
(518)385-8636
"Two-Dimensional Protein Crystals"

Professor George M. Whitesides
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138
(617)495-9430
"Overview of Opportunities in Bio-Chemical Technology"

Professor Mark S. Wrighton
Department of Chemistry, Rm. 6-335
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
(617)253-1597
"Chemical Based Microelectrode Devices"

Dr. F. Eugene Yates, Director
Crump Institute for Medical Engineering
University of California
Boelter Hall 6417
Los Angeles, California 90024
(213)825-4111
"Biological Materials and Computers"

Professor J. Zemel
Department of Electrical Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104
(215)898-8545
"Chemical and Biological Sensors"

APPENDIX C

-ATTENDEES-

Integration of Solid State Electronics and Chemical and Biological Systems Workshop

July 16-17, 1984

NAME	AFFILIATION	PHONE NO.
M. S. Wrighton	MIT/MRC	(617)253-1597
Bruce Gaber	Naval Res. Lab	(202)757-4301
Richard Blakemore	Univ. of New Hampshire	(603)862-2250
F. Eugene Yates	Crump Institute	(213)825-4806
Laurel Benton	UCLA	(213)825-7429
E. Uzgiris	G.E. Res. & Dev. Center	(518)385-2632
Ralph G. Nuzzo	AT&T Bell Labs	(201)582-5486
Jay N. Zemel	Univ. of Pennsylvania	(215)898-8545
John K. Stille	Colorado State Univ.	(303)491-7602
Semih Erhan	A. Einstein Med. Ctr.	(215)456-7219
Terence Barrett	Naval Air Systems Cmmnd.	(202)692-7445
Robert Metzger	Univ. of Mississippi	(601)232-5336
Robert C. Hughes	Sandia Natl. Labs	(505)844-8172
George W. Parshall	DuPont	(302)772-3277
Jiri (Art) Janata	Univ. of Utah	(801)581-3637
John Hirth	OSU/MRC	(614)422-0176
Henry Ehrenreich	Harvard/MRC	(617)495-3213
Roy H. Kissinger	U.S. Gov't	(703)351-2065
Elie A. Shneour	Biosystems Res. Inst.	(619)453-2525
Dick Reynolds	DARPA	(202)694-1953
M. Brian Maple	UCSD, Dept of Physics	(619)452-3888
David K. Ferry	Arizona St. Univ./MRC	(602)965-3708
Angelo A. Lamola	AT&T Bell Labs	(201)582-2645
Ronald Gutmann	RPI/MRC	(518)266-6794
Leslie E. Cross	Penn. St. Univ./MRC	(814)865-1121
George Whitesides	Harvard	(617)495-5430
Kenneth Thames	CRDC/APG, Md.	(301)671-3729
John Neff	DARPA	(202)694-5500
John Hutchinson	MRC/Harvard	(617)495-2848
Ali Argon	MRC/MIT	(617)253-2217
Tom McGill	Caltech/MRC	(818)352-4549
R. M. Osgood	Columbia/MRC	(212)238-3750
H. G. LeDuc	J.P.L.	(818)354-2208
H. Joe	UCSD/SIO	(619)452-8722
Ira Skurnick	DARPA	(202)694-4750
Robert Hellwarth	USC/MRC	(213)743-6330

MICROFABRICATION FOR ELECTRONIC AND THIN ORGANIC FILMS

R. Osgood

These comments are directed toward the interaction of the Biotechnology Program with microelectronic materials research and development:

1) There is a clear and important connection between work on micro- sensors for chemical and biological systems and solid-state electronics. Basically, the microsensor program presents an ideal opportunity not only to build devices which are intrinsically interesting but also to test and experiment with devices containing entirely new material systems. Good examples of this point are transistors with organic passivating films and gates. Some of these unusual device structures may undoubtedly lead to novel devices for electronic applications.

Another very important aspect of this work is that it presents an opportunity for learning to fabricate device microstructure of organic films. Organic microfabrication is increasingly becoming an issue in microelectronics manufacturing. For example, ceramic chip carriers require that inter- layers be made of low dielectric polymers. New research in fabrication technology for organics such as deposition and dry and wet etching, which will be developed on the microsensors program, is of direct concern for future electronics research.

2) A particularly important consequence of the thin organic and biological films which are being developed by the Biotechnology Program is that they may form useful materials for electronics microfabrication: Films of photoresists are currently the standard tool in microfabrication. The specific qualities of these films, such as microstructure adhesion; and etching properties determine specifically whether a particular micro-fabrication

sequence can be performed. Biological and self organizing films offer a unique opportunity for controlling and adjusting these film properties. For example, it is possible, in principle, to tailor the adhesion of film molecules to certain surfaces and not others or to adjust the microstructure so that etching or development an isotropy are built into the material. The two-dimensional crystalline films may offer a structure which allows sharp patterning even on angstrom scales.

**SUMMARY OF OBSERVATIONS AND CONCLUSIONS
FROM MRC MEETING ON
MITIGATION OF COUPLING AND SHOCK WAVES
FROM INTENSE SINGLE PULSE LASERS**

C. M. Stickley

OBJECTIVE OF THE MEETING

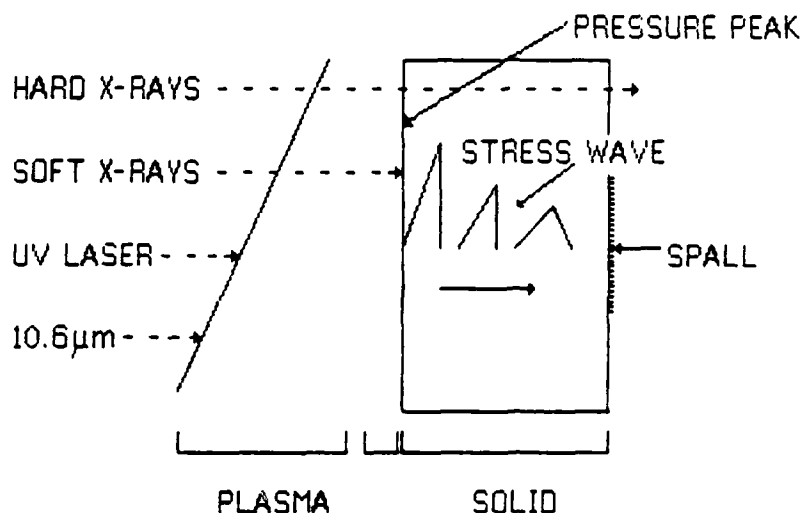
To determine if there are promising approaches to decoupling intense single pulse x-ray and UV/visible lasers from materials, and to reduce the shock which is transmitted through such materials to a substrate such as aluminum.

OUTLINE

- Introduction
 - Relative Laser Coupling & Phenomena
 - Estimate of Laser Produced Pressures
 - Research Areas for Various Photon Sources
- UV/Visible Laser Interactions
- X-ray Impulse via Surface Blow-off
- Stress Wave (Shock) Mitigation
- Spall Reduction & Interior Damage
- Conclusion
- Appendices
 - Case Study in Porous Be
 - Agenda for Meeting

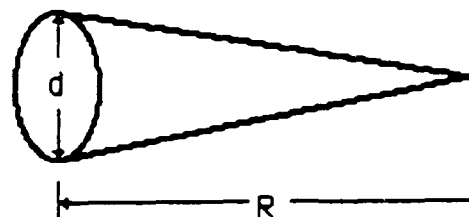
INTRODUCTION

Relative Laser Coupling & Phenomena



Estimate of Laser Produced Pressures

$$\begin{aligned}
 \text{Laser spot size} &= R\theta = R\lambda/d \\
 &= \frac{10^6 \text{m} \times 0.25 \times 10^{-6} \text{m}}{10 \text{m}} \\
 &= 2.5 \text{ cm}
 \end{aligned}$$



$$\text{Laser Energy Density} = 5000 \text{ J} / (2.5 \text{ cm})^2 \sim 1000 \text{ J/cm}^2$$

$$\text{Laser Impulse Coupling Coefficient} \approx 5 \text{ dyne sec/Joule}$$

$$\begin{aligned}
 \text{Impulse} &= \text{Coupling Coefficient} \times \text{Energy Density} = \frac{5 \text{ dyne sec}}{\text{Joules}} \times \frac{1000 \text{ Joules}}{\text{cm}^2} = 5000 \text{ Taps} \\
 &= \frac{5000 \text{ dyne sec}}{\text{cm}^2} \times \frac{1 \text{ bar}}{10^6 \text{ dyne/cm}^2} = 5 \times 10^{-3} \text{ bar sec}
 \end{aligned}$$

$$\begin{aligned}
 \text{Pressure} &= \frac{\text{Impulse}}{\text{Time}} = \frac{5 \times 10^{-3} \text{ bar sec}}{10^{-6} \text{ sec}} = 5 \text{ k bar for } 10^{-6} \text{ s} \\
 &= 0.5 \text{ Gpa} \\
 &= 75 \text{ Ksi} \\
 &= 5 \text{ Megabar for } 10^{-9} \text{ sec}
 \end{aligned}$$

Research Area for the Various Photon Sources

<u>Research Area</u>	<u>UV Laser</u>	<u>Soft X-rays</u>	<u>Hard X-rays</u>
• UV/Visible Interactions			
- Air to vacuum	x		
- Vacuum	x		
• X-ray Impulse via Surface Blow-Off		x	x
• Stress Wave (Shock) Mitigation	x	x	x
• Spall Reduction	x	x	x
• Interior Damage			x

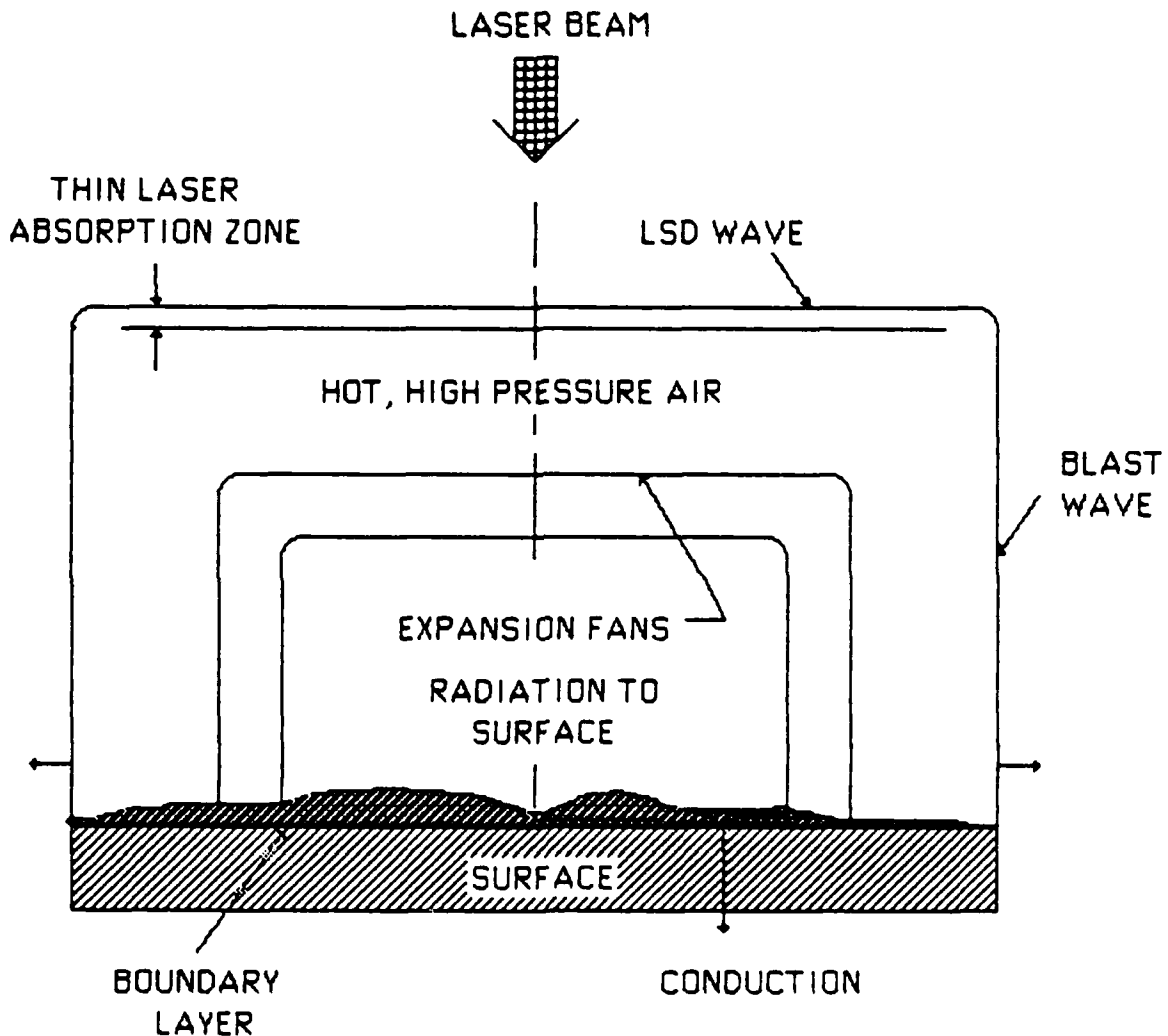
UV/VISIBLE LASER INTERACTIONS

<u>Materials/Hardening/Measurement Issues</u>	<u>One Atmos. to Vacuum</u>	<u>Vacuum</u>
• Materials data base	non-metals	metals plus non-metals
• Waveform effects	x	x
• Spot size scaling	x	x
• Discrete mass removal	non-metals	non-metals
• Effect of vapor on coupling	x	x
• Effect of air/plasma/environment	x	
• Impulse vs. increasing altitudes	x	
• Effects of load on coupling	x	x
• Hardening concepts: smoke, chaff, overcoats to control impulse	x	x
• Rep rate issues	x	x
• Analytic/computational "Loop Closing"	x	x

SINGLE PULSE LASER/MATERIAL INTERACTION DEPENDS UPON ENVIRONMENT

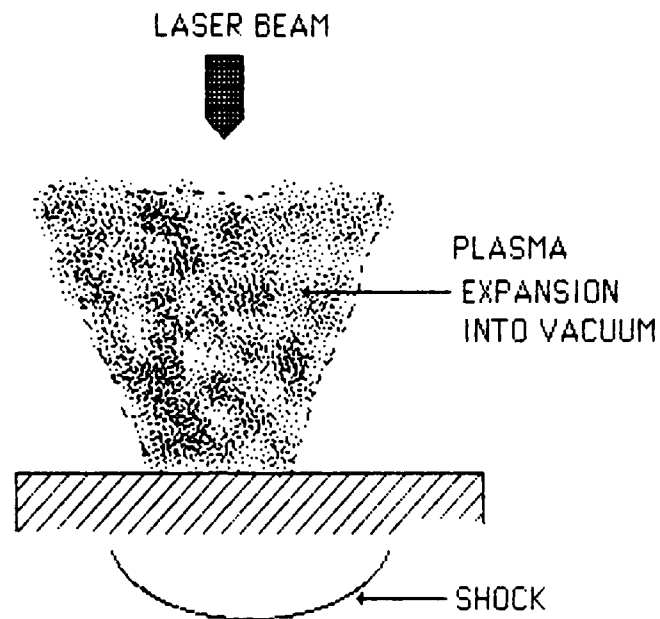
- ENDOATMOSPHERIC INTERACTION

(FLUENCE $\gg 50 \text{ J/cm}^2$, $\lambda = 0.35 \mu\text{m}$)



- PLASMA IGNITION: RESULT OF SURFACE IMPERFECTIONS (WAVELENGTH SENSITIVE)
- PRESSURE (AND ENERGY TRANSFER) MAY BE DOMINATED BY AIR GAS DYNAMICS
- IMPULSE COUPLING INSENSITIVE TO SURFACE MATERIAL AND WAVELENGTH

- EXOATMOSPHERIC INTERACTION
(FLUENCE $\gg 50 \text{ J/cm}^2$, $\lambda = 0.35 \mu\text{m}$)



- PLASMA IGNITION IN VAPOR (WAVELENGTH SENSITIVE)
- PRESSURE (AND ENERGY TRANSFER) FOR PULSE DURATION. PLASMA DYNAMICS UNCERTAIN
- IMPULSE COUPLINE DEPENDENT UPON MATERIAL AND WAVELENGTH

Facilities

- Co₂ versus UV laser coupling
- Availability of good beam quality, large pulse UV laser
- Large glass lasers (1.06 μ m) are available

Maximum diagnostics should be used:

Optical multichannel analyzers	Pulse Duration
Quartz discs for mass loss	Pulse Shape
Time-of-flight particle velocity	Laser intensity distribution
Streak photography	Plasma electron density
Fast pyrometers	Impulse measurement
- front surface	Incident and reflected pulse
- back surface	intensity

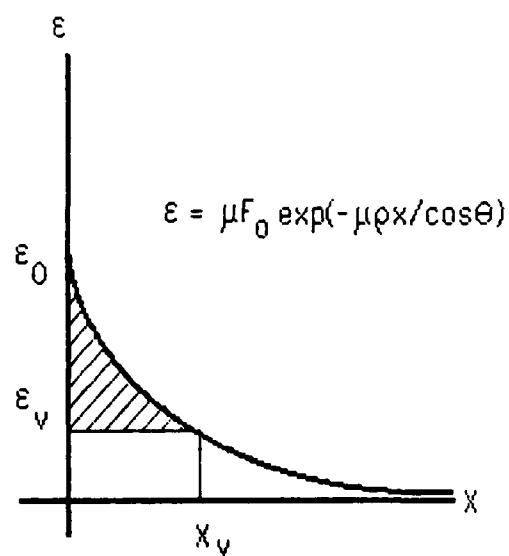
X-RAY IMPULSE VIA SURFACE BLOW-OFF

Need for Above-Ground Simulators Is a Primary Issue:

Approaches are:

- X-rays from a special synchrotron - Vineyard
- Exploding wires, imploding foils:
 - 400 to 800 J/cm² (100 to 200 cal/cm²) with debris
 - 200 J/cm² or less without debris
 - mildly adjustable spectrum
 - 4 to 6 shots per day
- UV lasers - Bloembergen
 - can simulate absorption depth and pulse duration of soft x-rays
- Large glass lasers: 40 J/cm² with no debris

ENERGY DEPOSITION



Calculated Energy Density at 1 KeV Necessary to Produce a Given Impulse

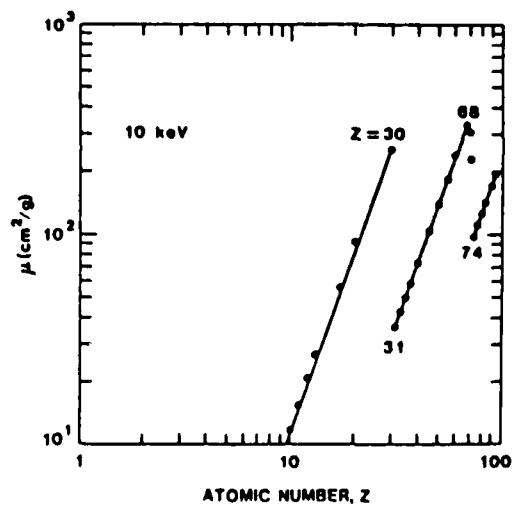
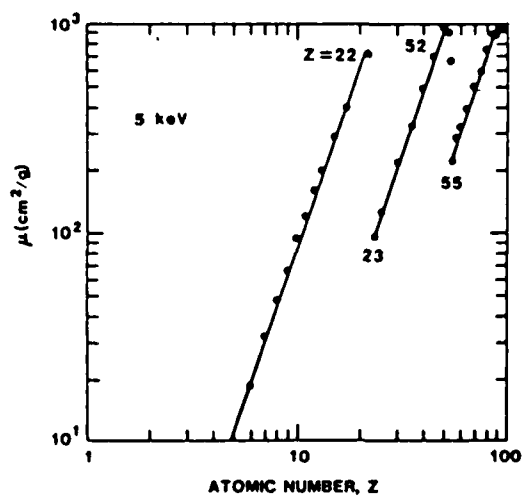
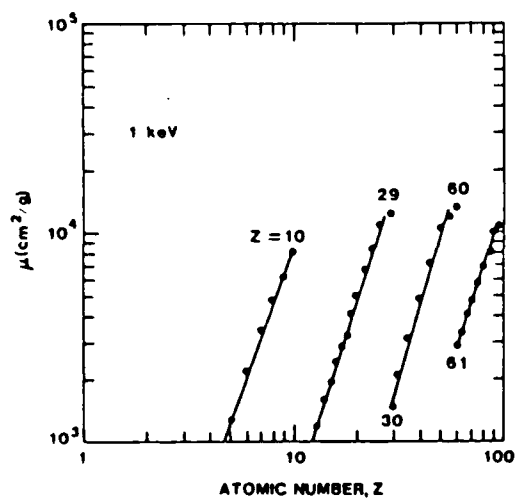
<u>Material</u>	<u>500 Taps</u>	<u>5000 Taps</u>	<u>50K Taps</u>
Beryllium	120 J/cm ²	650	20,000
Aluminum	40	650	40,000
Iron	50	5000	500,000
Gold	30	2000	300,000

Approaches to Reducing Impulse

- Geometric Attenuation
- Zero-impulse overlay
- Impulse deflectors
- Spin booster
- Materials development

Measurement/Materials/Hardening Issues

- Careful wavelength simulation
- Debris avoidance - perhaps by spinning shutter
- In situ techniques where possible
- Measurements and experiments to compare with impulse predictions
 - absorption vs. density (vapor region)
 - absorption vs. temperature
 - effect of high Z elements on impulse
 - design of multilayers
 - analytic models
- Materials development to reduce
 - a) blow-off impulse
 - control deposition profile
 - increase sublimation energy
 - cause off-normal incidence
 - b) peak stress
 - control deposition profile
 - provide low Gruneisen parameter
 - shorten acoustic relaxation time



STRESS WAVE (SHOCK) MITIGATION

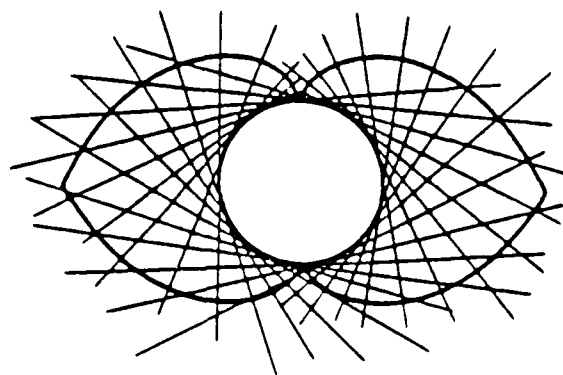
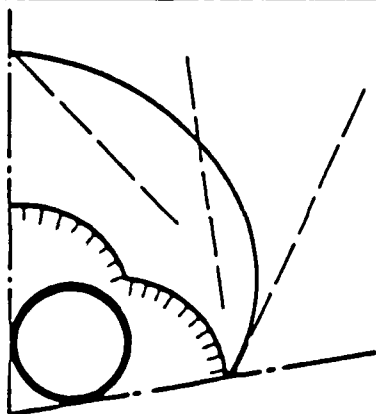
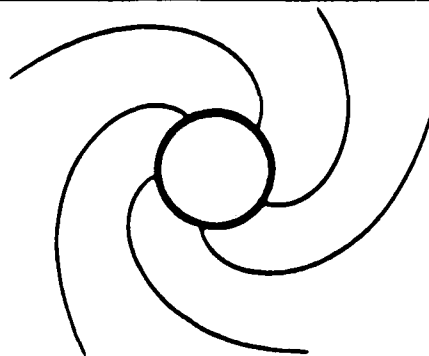
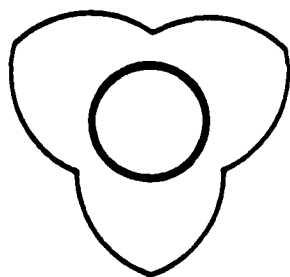
Approaches:

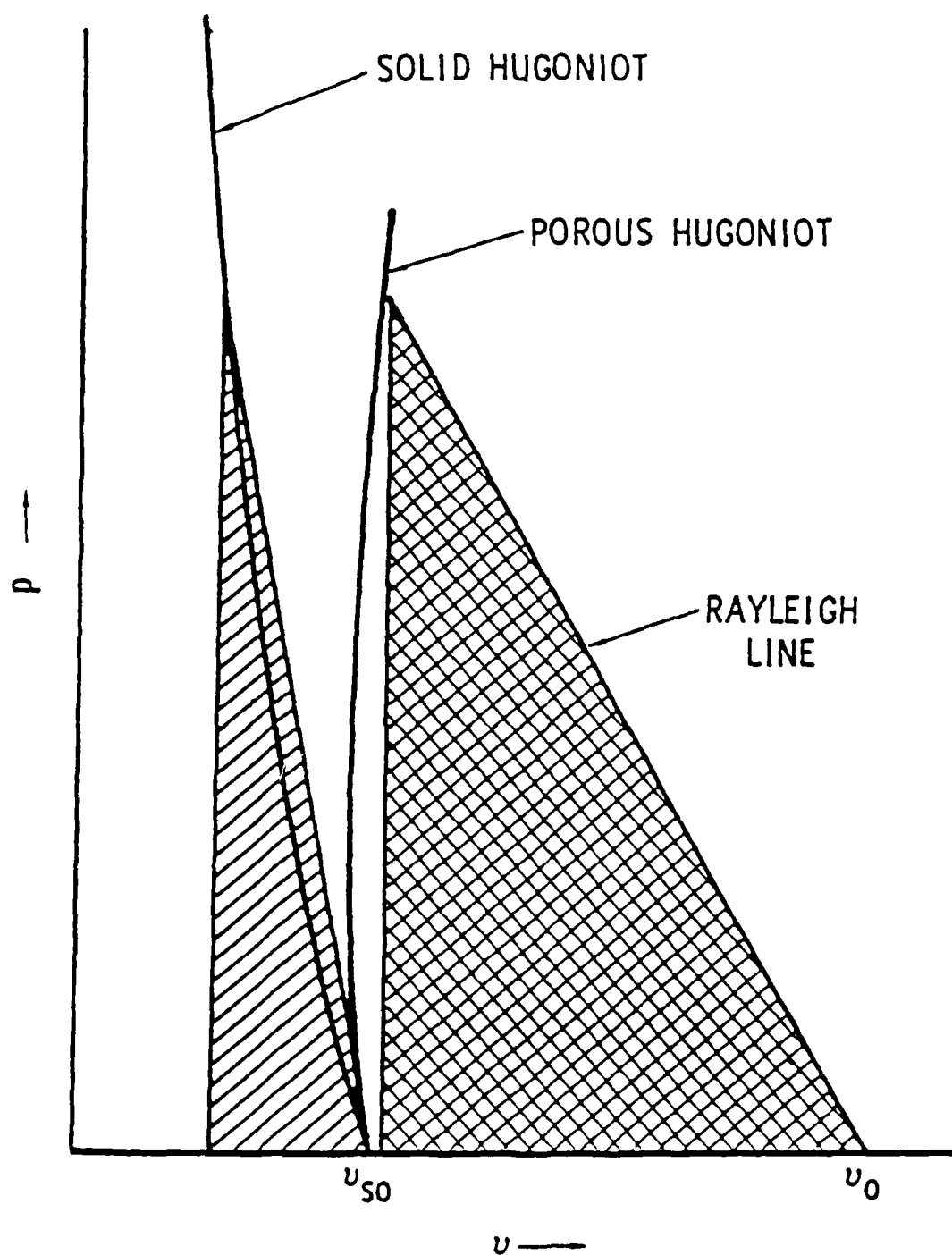
- Attenuation
 - porosity
 - viscoelasticity
- Dispersion
 - geometric designs
 - wave impedance mismatch
 - 3D composites
- Strength Increase
 - 3D composites

Issues

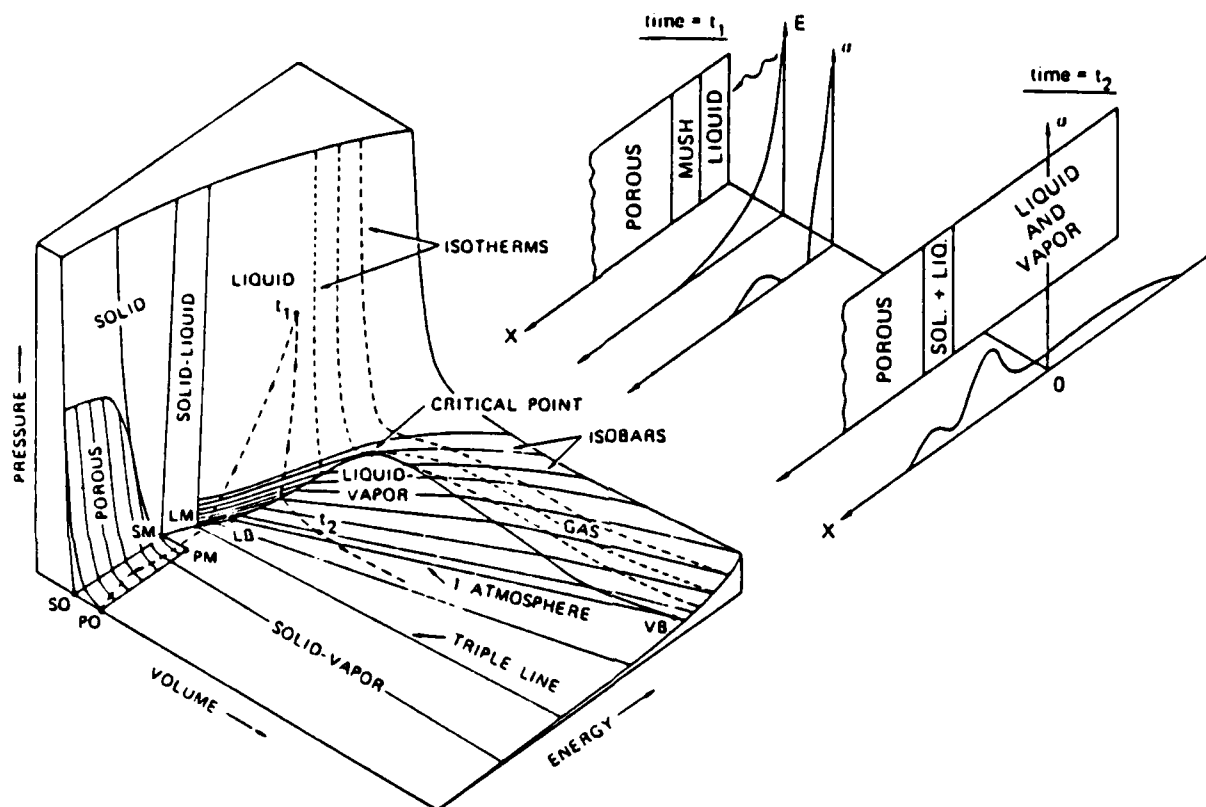
- Effectiveness of above approaches relative to each other
- Ability to predict performance of porous materials
 - modeling very complex
 - can do for a specific material
 - can't generalize; for example, many values of Gruneisen ratio for carbon - Hücke
- The use of single versus multiple layers of materials to protect against multiple threats
- The use of overlays versus 3D composites
- Other materials challenges
 - graded-through-the-thickness materials properties:
 - Z
 - melt energy
 - porosity
 - sublimation energy
 - shock impedance
 - Gruneisen ratio
 - impurity free plasma spraying techniques
 - lifetime in humid environment of porous paints
 - 3D composite cost reduction
 - minimizing coefficient of thermal expansion
 - improved bonding techniques while minimizing incompatibilities in thermal expansion and shock impedance

IMPULSE DEFLECTORS





HUGONIOTS OF SOLID AND POROUS MATERIALS.



PRESSURE-VOLUME-ENERGY (P-V-E) EQUATION-OF-STATE SURFACE AND TIME-SAMPLED STRESS PROFILES FOR A POROUS OR FULLY DENSE MATERIAL (U)

Projections: With porous materials, a 30x or higher reduction in peak stress and a 4x or higher reduction in impulse might be achieved.

SPALL REDUCTION & INTERIOR DAMAGE

Spallation Reduction

Principle: Increase allowable peak stress by strengthening materials

Approaches are:

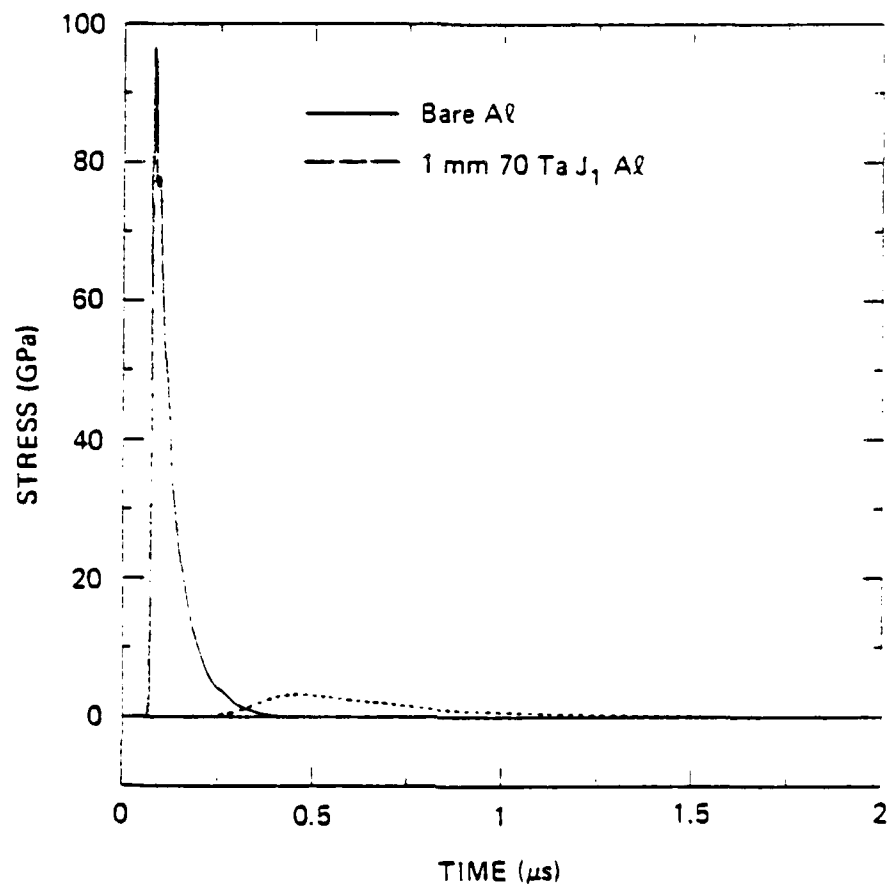
- add strong fibers in direction of maximum stresses
- increase strain-to-failure of composite materials by using tougher matrix materials (i.e., higher strain energy and strain-to-failure)
- 3D materials
- metal matrix composites

Interior Damage

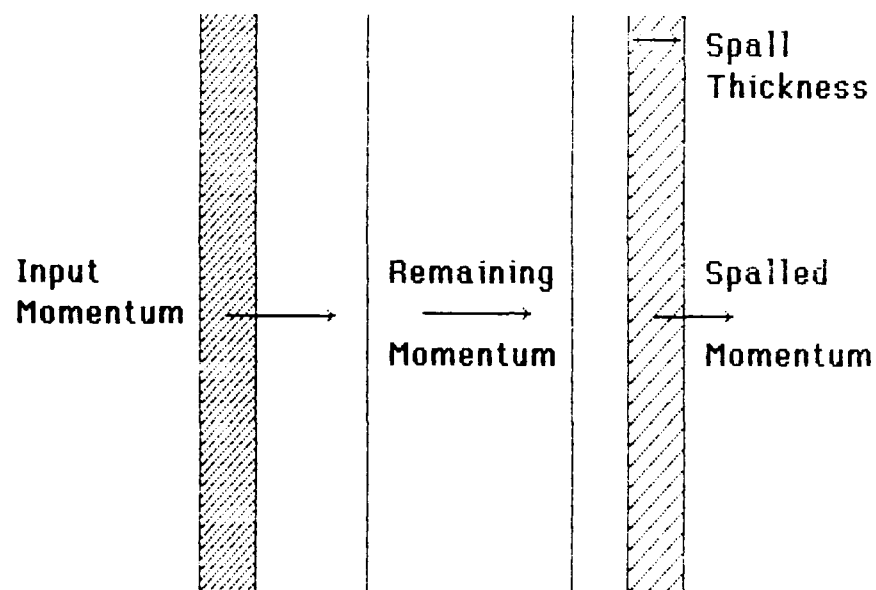
- Source: Hard X-rays
- Hardening concept: Distribute high Z elements throughout layers of materials to gradually absorb hard X-rays
- Tradeoffs: Spatial rate of absorption, shock generation, weight increase

PROTECTIVE COATING(S) PERFORMANCE REQUIREMENTS

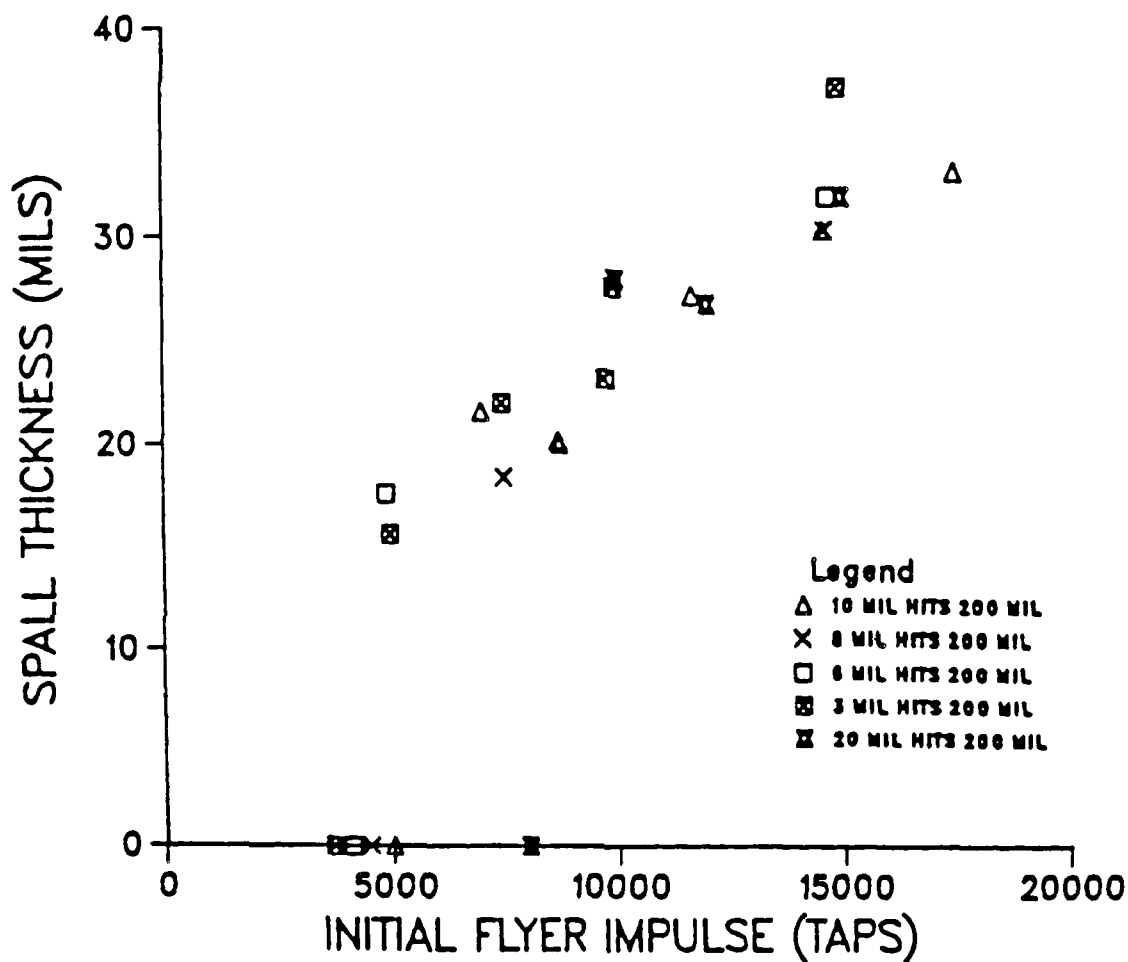
- Inhibited coupling
- Low density
- Controllable splash-off and blow-off
- Controllable opacity
- Shock Attenuation
- High spall threshold
- Multiple exposure capability

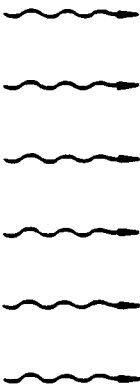


COMPARISON OF STRESS HISTORIES 1 mm IN DEPTH
FOR ALUMINUM TARGET EXPOSED TO SPECIAL
SOURCE WITH AND WITHOUT 70 Ta J₁ OVERLAY



SPALL THICKNESS INCREASES AS INPUT IMPULSE INCREASES FOR 6061 AL FLYER AND TARGET



Incident Radiation	Layer				
	1	2	3	4	
	Porous, low-atomic-number metal mixed with chopped refractory fibers (reflector, smoke generator, and scatterer)	High porosity ceramic or IMC (insulator and possible channel for coolant gas)	Loaded, porous IMC (x-ray shield)	Bond (adhesive and shock coupler)	Substrate

Laser shield,
 both pulsed and CW effects,
 relatively transparent to x-rays

X-ray
 shield

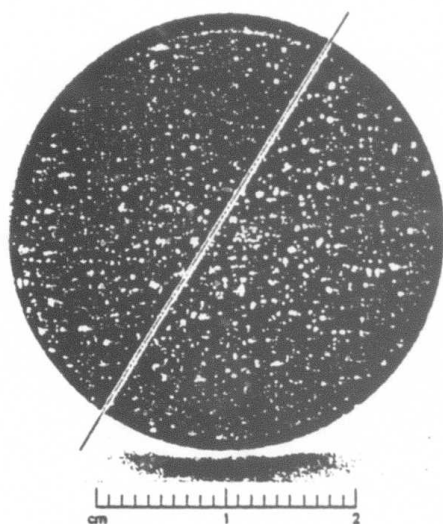
PROPOSED DESIGN CONCEPT FOR LASER ARMOR

CONCLUSIONS

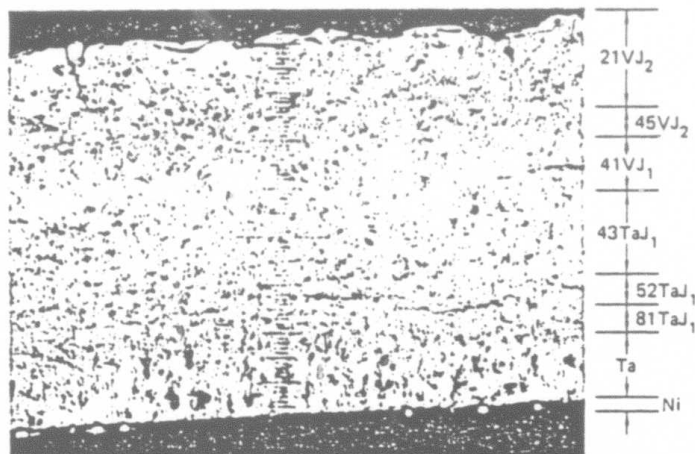
- There are many basic effects in UV/visible laser and in soft x-ray laser surface interactions which need to be explored and understood.
- Shock wave generation and possible techniques for mitigation of the shock are common to both of the above sources.
- There is a body of experience in 3D composites and porous materials which has not been fully evaluated.
- There are unevaluated approaches to minimize the impulse from UV and x-ray lasers, and to achieve significant attenuation of the resulting shock waves.
- Basic phenomenology and hardening efforts should be pursued to establish the maximum practical limits to hardening.

APPENDICES

- A. Quotes, comments and conclusions from a case study in porous beryllium:
W. M. Isbell, O. R. Walton, F. H. Ree, "Behavior of Porous Beryllium Under Thermomechanical Loading" UCRL-51682, Part 1; December 1977; supported by the Defense Nuclear Agency.
- B. Agenda for Meeting
- C. Attendees
- D. Recommendation for DARPA Program in Materials Development for Shock Hardening, N. Bloembergen
- E. The Potential of a Synchrotron Radiation Test Facility for Producing Intense X-ray Pulses, G. H. Vineyard



NOTE : Aluminum debris on front surface.



FRONT SURFACE AND CROSS SECTION OF IRRADIATED
GRADED-ATOMIC NUMBER OVERLAY SHOWING INCIPENT
SPALL AND FRONT SURFACE EFFECTS

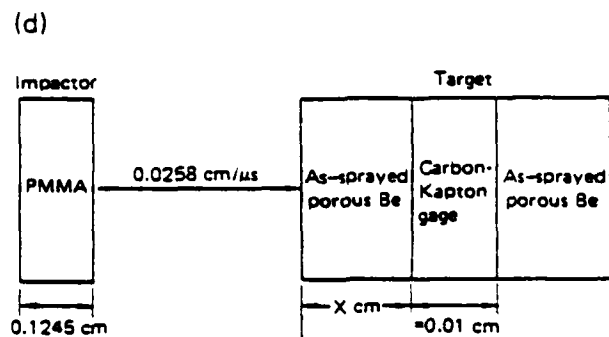
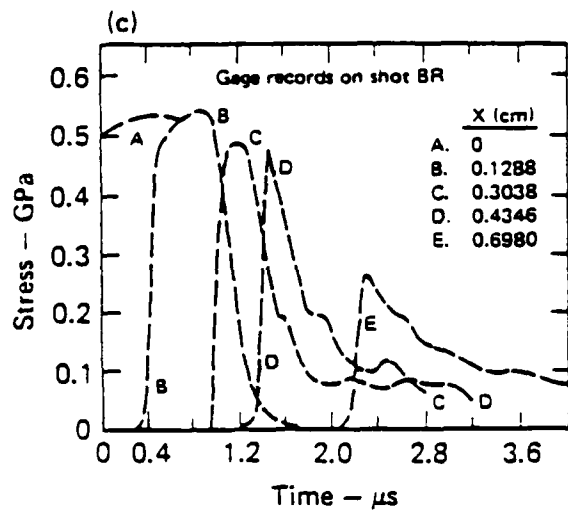
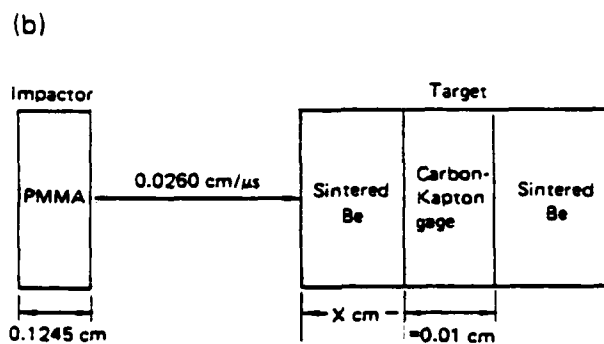
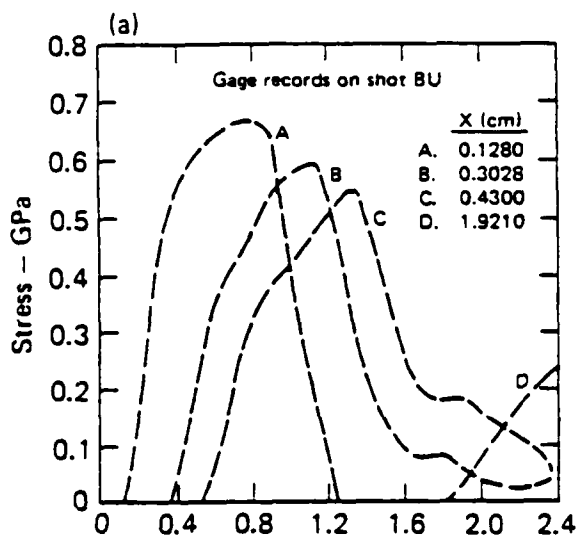
Porous Materials - A Key Approach to Shock Mitigation:

The State of Knowledge is Limited

Quotes, Comments, Conclusions from a Case Study* on Beryllium:

- The "bottom line": sufficiently accurate modeling of the complete response of specific materials can be achieved. It requires a great variety of material data; The modeling is also very complex.
- General comments on porous materials:
 - no unique EOS relations exists (pg 5).
 - comparing the GRAY EOS and Standard EOS for Be gives a 2.5 G Pa (25kbar), difference in predictions after pore closure. (Problem: absence of data on hot, expanded states of liquid Be) (pg. 9).
 - present measurement techniques do not provide data that "cover" the thermodynamic region of interest to designers of porous, protective layers (heating rates, energy - softening behavior, initial part of stress-generation curve; e-beam lacks shot-to-shot reproducibility, diagnostics at mid-to-high levels; so "interpret data carefully") (pg. 10).
 - the form of the dependence of yield strength on porosity is different (between two types of porous Be) depending on how the material is prepared. This is also likely to be true for metals other than Be. (pg. 6)
 - rate dependent pore collapse, leading to higher pressures than for near-static measurements, is difficult to predict a priori, or even to extend from rates adjusted to match those seen in a given flyer plate experiment. (pg. 6)

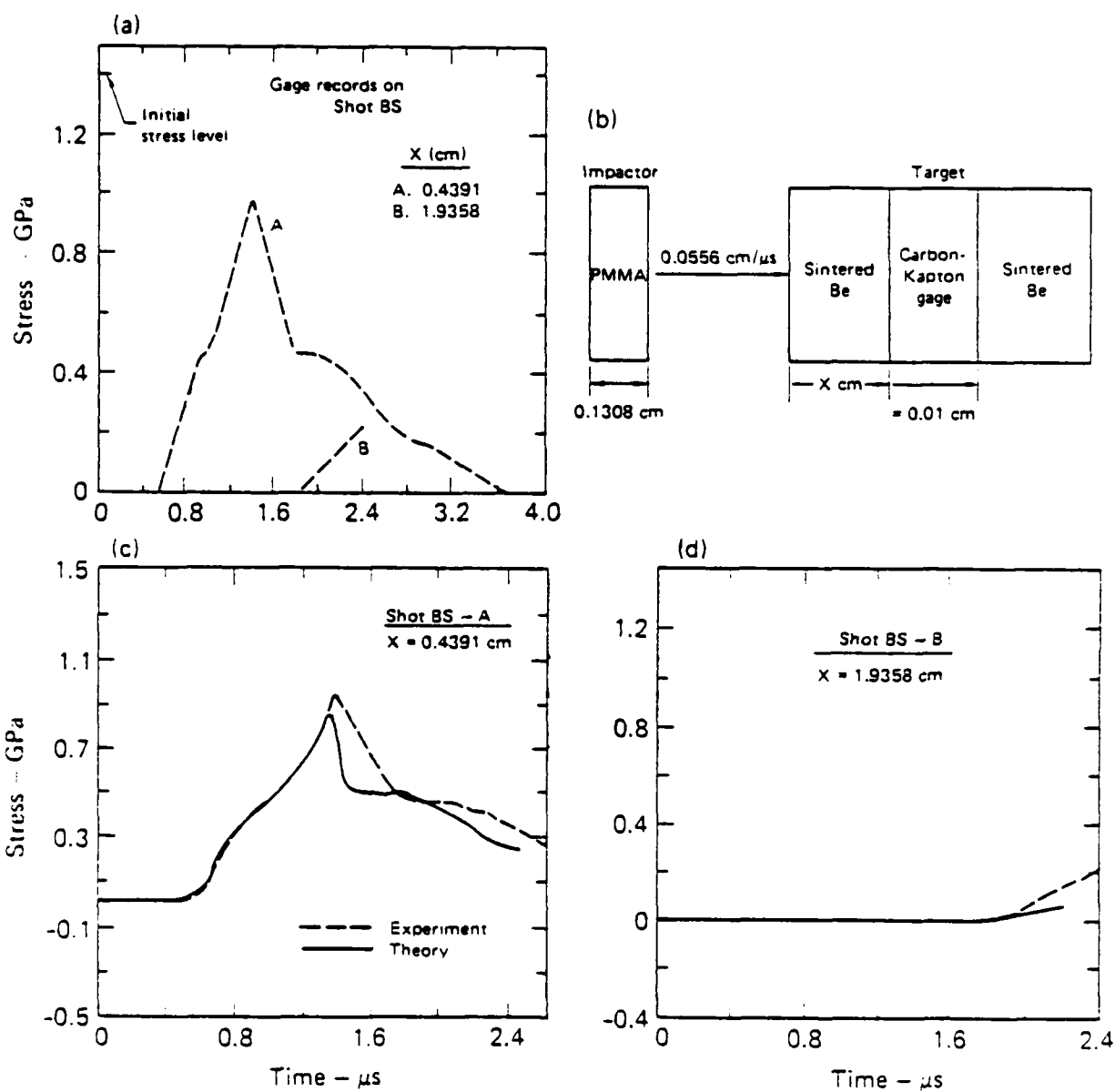
*W. M. Isbell, O. R. Walton, F. H. Ree. "Behavior of Porous Beryllium Under Thermomechanical Loading" UCRL-51682, Part 1; Dec. 22, 1977; supported by the Defense Nuclear Agency.



Measured development of compressive-wave system for sintered (a) and (b) and as-sprayed (c) and (d) porous beryllium.

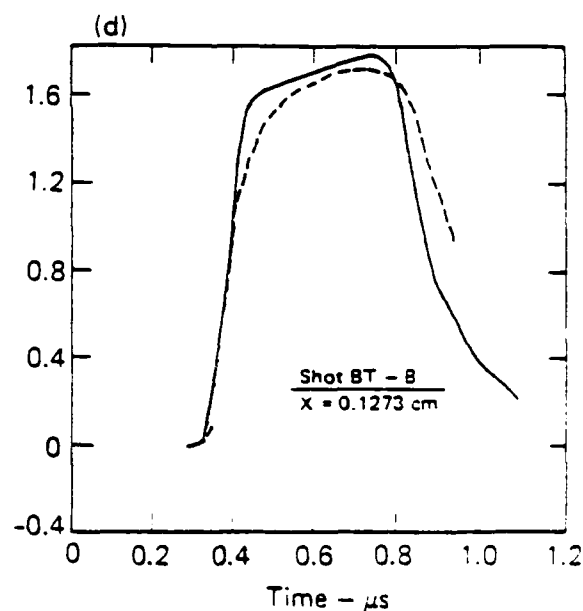
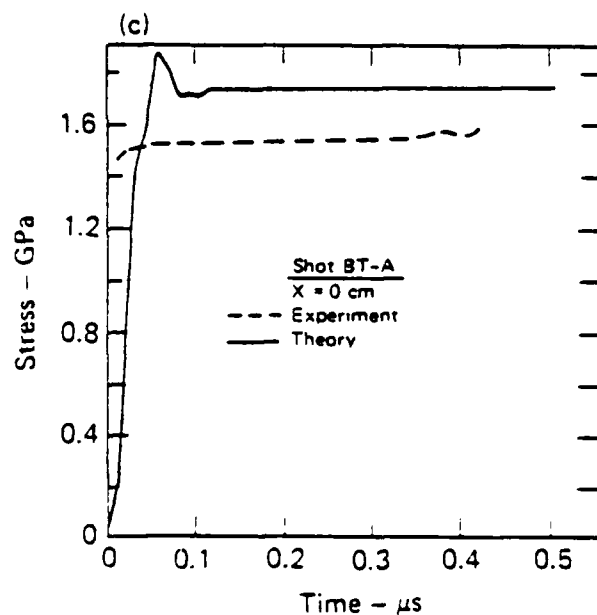
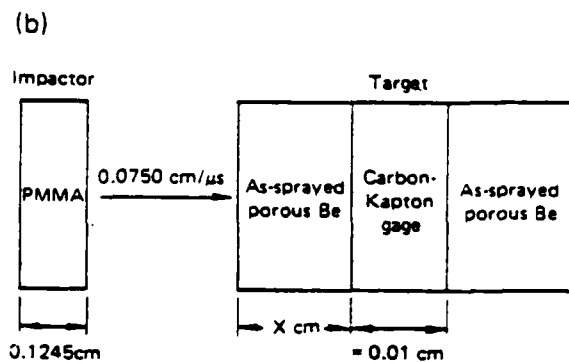
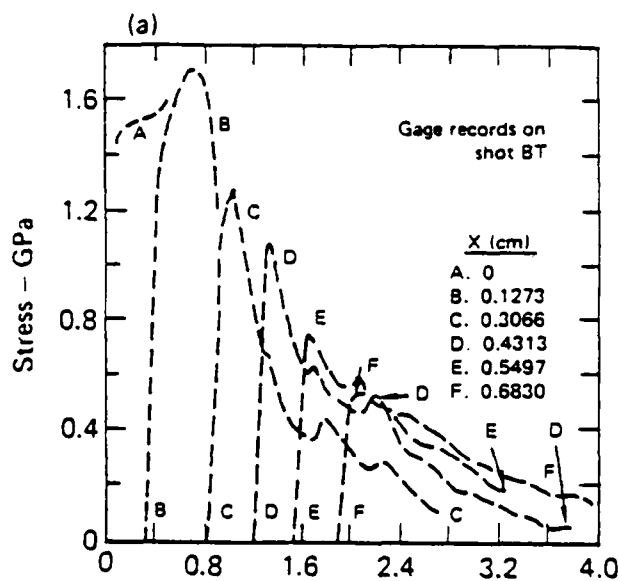
Comparing as-sprayed, porous vs. sintered, porous Be:

- axial stress, σ_1 , and stress from Hugoniot, σ_H , agree for one material but not the other.
- from e-beam measurements, significant differences exist in their stress-generation properties.
- faster-rising shock front and lack of an elastic precursor are two significant distinguishing features in compression profiles in as-sprayed versus sintered Be.
- Other Comments:
 - "currently little is known about the speed with which metals lose their strength when they are rapidly heated to near (or beyond) melting. If significant strength remains for a fraction of a microsecond after the material is heated near or slightly beyond melting, the pressure could be affected." (pg. 20).
- Comments on the model:
 - Application of their model to greater than 4 G Pa (40K bar) is "subject to uncertain error." (pg. 16)
 - "Accuracy of the model exceeds the level of the errors in the initial conditions that exist immediately after energy deposition from the pulsed e-beam source." (pg. 20)
 - "If Be of another porosity were to be considered, new static and possibly dynamic data would be necessary to calibrate the model for that material." (pg. 20)
 - "If a single model were to be used to describe 'porous Be' and the specific manufacturing and heat treating techniques used in its production were unknown, the resulting accuracy would be considerably less than that obtained in this work." (pg. 20)



Attenuated wave profiles of the high-stress shot (BS) for sintered porous beryllium (Be): (a) experimental gage records, (b) impactor-target geometry, (c)-(d) comparison of measured and computed wave profiles of different target thicknesses.

- "Generalization of the model to handle material with differing initial porosities or manufacturing processes could be achieved with a minimum set of laboratory tests. However, to obtain accuracy ... equivalent to the present work would require calibration to dynamic tests." (pg. 22)



Attenuated wave profiles of the high-stress shot (BT) for as-sprayed porous Be: (a) experimental gage records, (b) impactor-target geometry, (c)-(d) comparison of measured and computed wave profiles at different target thicknesses.

AGENDA

MATERIALS SHOCK AND COUPLING MITIGATION IN PULSED PHOTON INTERACTIONS

July 16-17, 1984
1200 Prospect Street
La Jolla, Ca 92037

MONDAY, July 16

Review of Shock-Mitigation Physics, W. Herrman, Sandia-Alb.
Coupling Difference Between Sources: Impact on Materials Design, W. Bookless, LLNL
Special Carbons: Physics and Modeling, G. Gurtman, S-Cubed
Special Carbons: Materials Development and Test Results, H. Berkowitz, MDAC
Materials Performance Requirements, Cermets, and Obscurants, D. Curran, SRI
Insights from Nuclear Explosion Containment Studies, R. Kidder, LLNL
Recent Efforts and Future Plans in Shock Mitigation Materials Development, L. Bertholf, Sandia/Livermore
Shock Mitigation Materials Concepts, E. Fitzgerald, APTEK
Shock Mitigation Materials Concepts, J. Kirby, MDAC
Approaches to Shock Mitigation, E. Oran, NRL

TUESDAY, July 17

Shock Waves in Metal Powders, T. Vreeland, Cal. Tech (an unclassified presentation)
Laser Induced Shock Effects in Metals and Composites, A. Clauer, Battelle
State of Knowledge in Pulsed Laser Coupling, A. Pirri, PSI
Role of Plasma Creation in Spoiling Coupling, D. Nagel, NRL
Plasma Effects; Smoke and Obscurants, R. Dingus, LANL
Discussion

Note: Jay O'Neill of AVCO, Wilmington, Mass, briefed members of the council on "AVCO X-ray Effects Experience for Laser Hardened Materials Studies" on July 25, 1984 in the SAI facility.

ATTENDEES

MITIGATION OF COUPLING AND SHOCK WAVES FROM INTENSE SINGLE PULSE LASERS

July 16-17, 1984

James Gee	Aerospace
W. E. Snowden	DARPA
C. W. Martin	DNA
D. J. Nagel	NRL
William Bookless	LLNL
Larry Bertholf	Sandia
B. Budiansky	MRC/Harvard
R. Hughes	NRL
E. Oran	NRL
E. A. Fitzgerald	APTEK
S. G. Wax	DARPA
Allan Clauer	Battelle
N. Bloembergen	MRC/Harvard
F. W. Patten	DARPA
J. S. Kirby	MDAC
J. L. Margrave	MRC/Rice U.
R. S. Dingus	LALL
M. J. Sinnott	MRC/U. Mich.
E. E. Huckle	MRC/U. Mich.
B. A. Wilcox	DARPA
C. I. Chang	NRL
R. Kerber	DARPA
P. S. Aminmoto	Aerospace
G. Gertman	S-Cubed
W. T. Barry	Aerospace
R. Kidder	LLNL
J. C. Williams	MRC/Carnegie-Mellon
D. Curran	SRI
J. D. Weisner	Lockheed
G. Vineyard	MRC/BNL
C. M. Stickley	BOM
A. N. Pirri	PSI
Harvey Berkowitz	MDAC
W. Herrman	Sandia
Franklin Serduke	LLNL

RECOMMENDATION FOR DARPA PROGRAM IN MATERIALS DEVELOPMENT FOR SHOCK HARDENING

N. Bloembergen

A basic test program for materials testing of UV Laser Pulse Interactions must be instituted with high priority.

Excimer lasers to carry out such a program with small scale, quantitative tests are already available. Larger scale tests will be possible with the next generation of excimer lasers.

These tests may also simulate impulse damage from soft x-ray lasers, as the absorption depth and pulse duration of UV pulses can be tailored to be comparable to those of the x-rays. This will be an efficient, fast and economical way to assess shock wave hardening.

The following parameters should be varied in a systematic manner:

1. UV absorption depth.
2. Surface roughness.
3. Investigate the influence of high Z-elements in carbons on UV impulse.

Under 1 consideration should be given to a UV protective overcoat to increase the UV absorption depth, compared to that of metal bearing carbons, to decrease impulse transfer. Under 2, the surface roughness could be made larger than the UV absorption depth. This would spread out flow-off material in different directions and also reduce the impulse normal to the structure.

The test should be fully instrumented and not be limited to impulse coupling and shock attenuation.



Other quantities to be measured include:

- a. Surface temperature vs. time
- b. Material evaporation and blow-off
- c. Backface temperature vs. time
- d. Incident fluence
- e. Pulse duration
- f. Reflected pulse intensity
- g. Momentum
- h. Plasma properties.

THE POTENTIAL OF A SYNCHROTRON RADIATION TEST FACILITY FOR PRODUCING INTENSE X-RAY PULSES

G. H. Vineyard

The effects of very short, very intense bursts of x-rays on materials and components are of continuing interest. Virtually all realistic experimentation has been confined to underground tests, which are difficult and costly, because the requisite intensities are not available from other sources*.

I suggest that modern accelerator technology and recent experience with synchrotron sources make it conceivable that a synchrotron radiation source could be built which could provide pulses of ultraviolet light or soft or hard x-rays of 10^{-8} second duration, or less, at intensities of the order of 10^3 Joules, or more, on targets of the order of 1 cm^2 in area. The spectrum could be controlled over a wide range of wavelengths and could be broad or narrow band. The targets would be accessible, and the repetition rate could be one per second or higher. For most purposes the rate at which targets can be mounted, rather than the capability of the machine, would limit the frequency of bursts; the effects of multiple bursts on one target could also be investigated easily.

A potent machine of this kind would not be cheap, if designed to the limits of present technologies, but its cost would not be unreasonable on the scale of costs of only a few underground tests.

The machine would consist of an electron accelerator injecting intense bunches of ultra-relativistic electrons into a series of bending magnets. The synchrotron radiation process produces an intense burst of

* High intensity pulsed lasers in the optical and infra red which energize targets are beginning to contribute to some degree.

electromagnetic radiation as the electron bunch follows a curved path in each magnet. The burst of radiation is contained in a fine cone centered on the tangent to the curved path. If the electron energy is E and $\gamma = E/mc^2$, where mc^2 is the rest energy of the electron (512keV), the radiation cone has an angle in radians of the order of $1/\gamma$.

For the sake of illustration suppose $E = 106\text{eV}$. Then $\gamma \approx 20,000$, and the angular cone has an intrinsic spread of about $1/20,000 \text{ rad} \approx 1/5 \text{ arc minute}$. Because of the range of directions in the finite arc through the magnet, this angle can be enlarged as desired. If it is not enlarged in this way, the beam of synchrotron radiation attains an area of 1 cm^2 at a distance of 200 meters (assuming that the beam cross section itself is small). A long vacuum pipe connects the source with the specimen. Actually a series of bending magnets alternating in polarity would be used instead of just one. This causes the electrons to follow a serpentine path and to produce a total burst of radiation which is much more intense. Such a device is known as a wiggler or an undulator. There is no obvious reason why it could not be long enough to extract a large fraction of the initial energy of the electron bunch.

If the bunch is 3 meters long the pulse of radiation will last 10^{-8} sec, and this remains true even if a long wiggler or undulator is used because the electrons are travelling very close to the speed of light.

If the bunch contains 10^{13} electrons, which is in the range of sizes of electron bunches in existing synchrotrons, its total energy would be 1.6×10^4 Joules. Extracting 10% of this and depositing it on a target of area 1 cm^2 then leads to the very interesting intensity of 400 calories/ cm^2 . Higher intensities would be produced at closer distances; the smaller areas limit

the experimental potential somewhat, but could still be of great importance. The assumption of 10^{13} electrons in the bunch is nominal, and it is plausible that larger bunches and proportionally higher intensities could be achieved.

The spectrum produced by a wiggler is the characteristic synchrotron spectrum, a smooth curve with a peak intensity near a characteristic wavelength* λ_c , falling off sharply at shorter wavelengths and more slowly at longer wavelengths. It is not a Planck spectrum, but it is not enormously different from that, mainly departing because of the slower fall off at long wavelength. The critical wavelength, is give by

$$\lambda_c = 186.4/B E^2$$

where B is the strength of the magnetic bending field in kilogauss, E is the electron energy in GeV, and λ_c is in Angstroms. If $E=10\text{GeV}$ and $B=1$ kilogauss $\lambda_c = 1.86\text{\AA}$.

A coherent wiggler, or undulator, alters the spectrum by emphasizing one or more characteristic wavelengths. Virtually a line spectrum of adjustable wavelength is theoretically attainable.

The bunch length can be varied to produce pulses of variable duration. At a cost of reduced intensity, pulses of 10^{-9} sec duration would be easy to provide, as would pulses longer than 10^{-8} sec up to a limit set only by the design of the source. A quasi-dc source could be provided if desired.

The source of electrons would most likely be a synchrotron with a linac injector, possibly mediated by a booster ring, but many design variations are possible. The optimum design, detailed limits of capability, and realistic cost estimates could only be provided by a design study of

*Half the total power is radiated above λ_c , half below.

considerable scope - say half a dozen people working for 3 to 6 months. In general the cost will increase rapidly with the electron energy and the size of the electron bunches desired. The illustration above of 10GeV might suffice for most purposes. In general the intensity will increase with increasing energy in this range because at higher energy more electrons can be forced into the bunch. If pulses are desired only at intervals of an hour or more, economies in the design might result, although this is territory well outside the parameter range of existing electron accelerators. Much ingenuity in the radiator design (wiggler or undulator) is conceivable. Spectral shaping within wide limits, for example, should be possible. Also a series of wigglers, with the electron beam deflected a few degrees after each one, could provide a series of x-ray beams, of increasing wavelength, on separate targets simultaneously.

Such a machine might also be of use for studying the interaction of intense charged particle beams with the atmosphere. If the injector is a circular machine, it could readily be used for free electron laser experiments in addition to the foregoing program.

To my knowledge, no serious consideration has yet been given to building a machine of this sort.

OPTICAL INTERCONNECTS IN COMPUTER NETWORKS

A. Yariv, D. K. Ferry, R. J. Gutmann, R. M. Osgood, A. Macleod
and R. W. Hellwarth

INTRODUCTION

In large computer systems today, the interconnections between chips, boards, and modules are both extensive and a limiting factor to further development of the technology. As these systems evolve, the interconnection problem will become ever more burdensome, since delays encountered by sending signals over these circuits eventually limit the processing speed of the network itself. Optical interconnection technology offers the possibility of contributing significantly in this aspect of future computer networks.

Future computer systems include general purpose machines, super-computers, special-purpose signal processors, microprocessors, and symbolic logic processors. The interconnection requirements differ among these machines, but will remain a severe problem in large processors (such as multiple chip processors containing densely packed electronic circuitry). The key factors in the interconnection issue include the following:

- distance between interconnections,
- delay and rate requirements, and
- serial/parallel nature of signals.

In view of the above considerations, the MRC hosted a two-day meeting on July 18-19, 1984 in which the general status of materials, devices, and strategy was discussed. The program and list of attendees are attached as Appendices A and B. This meeting brought together, possibly for the first time, experts on computer design, optoelectronic devices, and high speed optical transmission.

The intent of the meeting was to hear about major (present and anticipated) problems in computer design which are due to interconnect difficulties, to learn about the state of the art in high speed optoelectronic devices (semiconductor lasers, modulators, detectors, and switches) and then consider how the application of optoelectronic techniques might alleviate interconnection problems. Another purpose of the meeting was to consider how the application of real time holographic techniques might lead to a new generation of reconfigurable computers.

In what follows, we present a synopsis of the meeting, the discussion which occurred, and our observations, conclusions, and recommendations.

MEETING HIGHLIGHTS

Optical interconnections will evolve along established patterns that involve moderate distances and high bandwidths. Bandwidth requirements on interconnections in computers will continue to increase. There is also some feeling among the computer community that interconnection distances will also continue to decrease to the point of chip group interconnections, especially as VLSI implementations become more prevalent. On the other hand, long interconnections are now made with bulky coaxial cable, and the replacement of this bulky, multi-conductor cable with optical multiplexed signals on a fiber would have economic advantage if achieved at a relatively low cost.

It appears that a number of material systems are available, but that considerable problems still remain. The work directed at integrated optoelectronic systems with lasers/detectors and digital multiplexers is most pertinent, and seems most advantageous when achieved upon a single

integrated chip. However, semiconductor processes which are consistent with both electronic and optical devices must be defined and developed for this to be achieved. Even so, it is likely that the optical systems will continue to be hybrid "add-ons" to the current and proposed GaAs VLSI systems for some time to come, so that considerable packaging integration problems must be solved. Several pertinent efforts are addressing this problem, however, and the work reported by Leonberger (Lincoln Labs) and Carney (Honeywell) stand out as being particularly germane to the issue. The difficulties of actually implementing the attractive concepts presented during this meeting can only be discovered by building and testing working hardware and by interfacing it to other components of the system at an early time. Lau (ORTEL) described extreme high speed ($f > 116\text{Hz}$) modulation of semiconductor lasers. This high speed is made possible by a new laser design which incorporates epitaxial transparent end sections ("windows") which make it possible to run the laser at the increased power levels needed for high speed modulation. He also indicated that considerably higher modulation speeds should result from the incorporation of quantum well configurations in future lasers.

Also noteworthy, although not exactly in the scheme of optical interconnection technology, was the presentation of D. Bloom (Stanford) on the use of picosecond laser pulses to measure signal propagation in digital electronic circuits. The future applications of this technology to general metrology, circuit testing, and fault sensing are evident, but still must be fully developed.

The long-term prospects for optical interconnections are very exciting. The prospects of reconfigurable interconnects opens the door to

new types of computers and divergence from the current philosophy of computer design in general. No experimental work or an analysis of reconfiguration devices was presented so that the field is currently too young for us to assess its viability or to be able to forecast a particular direction, but the presentations of Lipovski (Texas) and Tanguay (USC) were especially germane in their illumination of future prospects. In particular, future computers with highly dispersed computing elements will need to take advantage of very-high speed and reconfigurable interconnects if they are to become truly viable. Indeed, one speaker even ventured to say that the entire development of "fifth generation" supercomputers awaits the development of optical interconnects, and without this development, they may fail.

A separate topic in reconfigurable interconnects is the possibility of using the optical links for hierarchical control signals. Here, slower links can be used, but the prospects of the dynamically reconfigurable paths opens new horizons for tree-structure control of computer hierarchies.

OBSERVATIONS AND CONCLUSION

Interconnects can usually be categorized by the distance over which they transmit signals. In computers, we may generalize these as:

- intra-chip,
- chip-to-chip,
- board-to-board, and
- module-to-module

Intra-chip communications proceed over integrated transmission lines within a single LSI or VLSI chip. Advances in VLSI will probably cause this technology to surpass the currently utilized gate-arrays. The current

thinking on chip pins/connections is not applicable to VLSI, which results in vastly reduced numbers of pins required. Moreover, average interconnections within a chip are usually short, so that the impact of integrated optical links is not expected to be high. Consequently, the advantages of fixed on-chip or on-wafer interconnections by optical means do not seem to be sufficient to warrant such a technological effort.

Chip to Chip and Board to Board communications are two applications that can greatly benefit from the speed advantages inherent in optoelectronic techniques. The total communication rate in today's giant computers (say, Cray 1) is ~55 Gbit/s and in those of the next generation (Cray SMP II, for example) will approach 506 Gbit/s. This type of communication is handled in the present technology by a large number (~100) of parallel lines (channels) connected to each chip. This problem can be greatly alleviated by multiplexing the large number of parallel outputs to a single serial channel and using the combined bit train to modulate a single semiconductor laser. The output optical beam can then propagate in a fiber or in air. On the receiver side one would employ a fast detector and a demultiplexor to recover the individual parallel channels.

The implementation of these ideas will depend on the availability of integrated monolithic GaAs, or other fast semiconducting material, multiplexer-laser circuits and, on the receiving side, of integrated detector, demultiplexer circuits capable of operating in the multi-gigabit regime. Initial results for producing such integrated optoelectronic circuits were described but it is clear that such circuits are in their very infancy and although a number of integrated optoelectronic circuits have been described (Honeywell, Rockwell), the performance of the individual elements was far

short of the level needed for incorporation into computers. The major improvement needed here involve reduction of laser threshold currents, increase in the modulation speed, developing transversely emitting lasers, and the development of a GaAs processing technology which is consistent with both optical and electronic devices.

The presence of the GaAs foundry program provides particular direction here, and it is felt that efforts toward developing the appropriate GaAs based integration of multiplexers with sources/detectors will benefit from it's existence. The difficulties of actually implementing the attractive concepts this allows can only be discovered by test hardware being available for system test-beds. Problems of fabrication can also be investigated by utilizing the foundry availability.

In pursuing the above, future work should also consider techniques which are effective for parallel transmission as opposed to purely serial channels. Computer systems have internal parallelism, while most optical efforts have concentrated on serial channels. The very high speed advantages offered by the optical interconnects will not be fully realized if the parallelism inherent in computers is totally abandoned in interconnects. Multiplexing should be between channels, not for bit-serial transmission. This can be achieved for example, by an arrangement wherein each internal parallel channel is used directly to modulate one, monolithic, dedicated laser whose output is then carried away in a single fiber. (One will be able to use wavelength multiplexing to combine the outputs of several, say 5-10, lasers in a single fiber). For such an approach to become attractive, we need to develop a new generation of extremely low threshold (say 1 ma) lasers, but these will only need to operate at very modest ~6bit/s.

We have described above two extreme cases, i.e., full parallel-serial multiplexing and no multiplexing. Intermediate schemes using partial multiplexing might also prove attractive.

Most of the consideration of the section dealing with chip to chip and board to board communication apply as well, to communication between modules. An additional consideration here is that, in parallel computer networks, such modules can be separated by long distances exceeding possibly a few miles. In this case the full parallel or serial-mode of inter-connecting will require the use of long wavelength (1.3-1.5 μ m) lasers to avoid the problem of pulse spreading with the shorter wavelength GaAs lasers.

Reconfigurable Computers

The ability to dynamically reconfigure the interconnections between modules and between boards may have the largest impact on computer design. The basic idea here is to use optoelectronic switchyards (employing electro-optic crystals or photorefractive crystals) to redirect freely propagation (or guided) light beams so as to arbitrarily connect simultaneously any of N, (data drive) laser sources to any of M detectors. Such a capability would have a major impact on clock distribution, transmission, distribution of control signals, system reconfiguration and massively parallel memory access to name a few functions.

Our conclusion from the meeting and the study of the available literature is that the thinking in this area has not yet reached the stage of zero order feasibility studies. There has been, surprisingly, no attempt to ascertain if the required performance levels, which would be of interest to the computer designer in terms of the number of switchable beams, the reconfiguration time, cross talk, and switching efficiency, is achievable and is consistent with the basic physics of the proposed devices.

RECOMMENDATIONS

There is an important need for early and convincing demonstration of interchip and interboard optical interconnection. This should help sell the computer community of the practicality of these approaches, so that they can start including them in their thinking and in their designs. We have discussed above two approaches to interchip (board) communication:

(i) A scheme based on high level multiplexing of parallel electronic channels to one (or a few) optical channel by means of high speed GaAs electronic circuits driving a very high frequency GaAs laser.

(ii) A parallel scheme whereby an array comprised of a large number of low power relatively slow GaAs (or GaInAsP) lasers. Such an array need not await the development of integrated optoelectronic GaAs circuits since the driving and receiving circuits are all in silicon. The main emphasis here will be on extreme low threshold (say <10 ma) lasers and on the packaging of the output fibers and the driving lines.

The development of low threshold GaInAsP laser array is also recommended. These lasers emit at $1.3 < \lambda < 1.5 \mu\text{m}$ and will be needed when the interboard distances exceed a few km.

We also recommend that the research effort in GaAs/GaAlAs integrated optoelectronic circuits continue and, if possible, be strengthened. This development will be necessary in order to test the feasibility of serial multiplexing interconnects.

Discreet devices whose development is recommended are: (1) Ultra low threshold and high bandwidth ($>10\text{GHz}$) GaAs, GaInAsP lasers to handle extreme high rate data communication. (2) Integrated laser arrays driven in parallel by the (parallel) electronic signals.

Scheme (i) is the one presently pursued and its implementation depends on progress in the area of GaAs monolithic integrated optoelectronic circuits. Judged on the size of the effort, the size of the challenge, and the rate of progress, it is not likely that a serious demonstration of this approach, convincing enough to interest the computer designer, can be contemplated in the very near future.

Scheme (ii) is far less ambitious and can be carried out using a hybrid technology in which, assuming N parallel channels, the GaAs chip will contain N lasers and their low speed drivers.

We thus recommend a program to develop monolithic arrays of low threshold GaAs lasers for parallel interchip (board) connections. This array will be driven by relatively low speed, say 100MHz, silicon circuits.

In the area of reconfigurable interconnections we recommend at first a theoretical study to determine the needed performance requirements of the interconnection medium. Specific questions to be answered are:

- (1) What physical phenomena (electro-optic, photorefractive, acousto-optic, etc.) seem most promising?
- (2) What switching efficiencies are possible with these materials?
- (3) What is the anticipated crosstalk (due to scattering, defraction, etc.) and can it be tolerated?
- (4) What switching speeds are available from present day crystals and can they be modified by doping, intensity of radiation and otherwise to conform to system needs.
- (5) What are the problems associated with the existence, simultaneously of N optical beams and N gratings in the switching crystal.

If enough of the critical questions (1)-(5) posed above are answered satisfactorily, then it is recommended that an effort be undertaken to develop the switching medium and to demonstrate elementary interconnections.

DISCUSSION OPTICAL INTERCONNECT APPLICATION CONSIDERATIONS

H. M. Brauer

Optical interconnections will evolve along established patterns - moderate distances, high band widths. Band widths will increase; distances will decrease to the point of chip group interconnections. Chip-to-chip and on chip communications remain much further away in terms of practical application; full wafer structures will be common before the on "chip" techniques reach wide use in computer environments. Special application will come sooner.

Two areas look promising: 1) multi-processor/system switch connections with controlled free space techniques; 2) integration of optical emitters with electronic elements on the same chip. Both areas appear to be ready for research systems applications within a few years.

It appears that a number of materials systems (mixed materials) problems remain to be solved. Consistent semiconductor processes must be defined and resolved -- optics will continue to be "add-ons" to electronic processes for the next few generations of process development. Packaging integration is a major problem: today's packages are hostile to optical applications. Power and thermal effects have to be considered (low power and room temperature may not be requirements, but the effects should be understood). Some materials system reliability studies are appropriate before serious applications will emerge.

Electronic-optical package mismatches are a major problem today. Future work must include package development to exploit the optical capability. Future work should also consider techniques which are effective for parallel transmission as opposed to purely serial channels; computer

systems have internal parallelism. Most optical work has considered serial channels; a number of systems problems must be solved to achieve effective parallel transmission.

R. W. Keyes

Optical interconnection seems most useful for the long interconnections among different units of a computer system, e.g., disk drives to memory, CPU to disk drive, tape storage to printer. For the short interconnections within any of these boxes it has many disadvantages: the conversion of electrical signals to optical and back again to electrical takes time and delays the signal, it dissipates additional power in a place where removal of heat is already a serious limitation on the performance of the technology, and it adds cost where great cost-effectiveness has already been achieved in providing 10^5 or more of these short interconnections with conventional technology.

Long interconnections are now made with bulky coaxial cabling; replacement of multiconductor coax with optical signals multiplexed on to a fiber would have economic advantage if it can be done at low cost. Thus, the work directed at integrated optoelectronic multiplexers are most pertinent. The contributions of Carney (Honeywell) and Leonberger (Lincoln Labs) stand out in this regard. The difficulties of actually implementing the attractive concepts presented during the meeting can only be discovered by building and testing working hardware and by interfacing it to other components of the system at an early time. The factors that cause new technologies to fail are such things as sensitivity to temperature variations, low reliability, and inability to reproduce device characteristics, are not discovered by paper studies and are simply ignored in many optimistic projections.

It is worth pointing out, too, that some of the apparently novel concepts presented were known in the middle 1960's. Rutz demonstrated an optical transistor and a "translaser" in the early 60's. Nathan and collaborators reported optical bi-stability in a GaAs laser with an absorbing region in 1965. These experiments are conducted at cryogenic temperatures; however, the room temperature GaAs laser was realized in 1970. One cannot help but notice that not much has happened in these many years.

6. Jack Lipovski

There are three types of parallel computers: special purpose (e.g. FFT, finite element, etc.), general purpose inextensible (e.g. using busses, rings or crossbars) and extensible. The latter class includes TRAC, NYU Ultracomputer, Purdue's PASM, Illinois' CEDAR. They are capable of extension from N to Nel computers (almost) indefinitely, and thus will not require further research and development to extend them again in another few years. In this sense, they may be the most important 5th generation supercomputers. "Final generation computers" will have these architectures that use multistage interconnection networks which are exceptionally pin-intensive. These cannot take advantage of VLSI until the "pin problem" is solved. Optical interconnections seem to provide the best approach to provide enough bandwidth. Thus, the development of extensible fifth generation supercomputers awaits the development of optical interconnects, and without that development, they may fail.

Angus Macleod

It was fairly clear at the meeting that the computer people were some way from enthusiastic about the prospects of much help from introducing optical interconnections and I am inclined to agree with them. The near term possibilities suggested at the meeting were all considerable

complications, especially in the case of silicon. I thought that the observation that the potential of microwave links had not been fully exploited was a significant one. I cannot believe that the silicon people, in particular, would readily adopt the complication of optical fibres and the necessary gallium arsenide drivers just to save some pins. The tremendous advantage of optics in the near term appears to be in the enormous data handling capacity. But this technology largely exists, and I think that Wulf Knausenberger was right when he said that whether or not it would be used was now mainly a question of economics.

The long-term prospects on the other hand are very exciting. New types of computers, programmable interconnects, the breaking away from the present philosophy of computer structure are all possible. The field is too young to be able to pick out a single path which should be followed. Right now broad support of a wide variety of bright ideas is required with a critical review in a few years' time.

One aspect of all this that seemed to miss attention at the meeting, however, is the almost automatic statement that optical interconnects are not subject to interference (the electrical rather than optical measure). This is not true. Specular reflection, scattering, both bulk and surface, and diffraction, all cause interference. An insertion loss of 3dB for an optical compound seldom means that the 3dB loss does not simply vanish; it almost invariably goes somewhere else. The vision we were treated to of the vast bands of interconnecting wiring that drape the modern computers, the estimates of immense numbers of pins and chips and the predictions of programmable interconnection schemes all suggested quite large numbers of optical beams. In the long-term computer developments these beams will be mostly unconfined by fibre guides. With just a few beams we can expect

cross coupling to be fairly small but as the number of beams increases I expect the problems to become severe unless steps are taken to address them now. It may be that this is being done but I got no sense of that from this meeting. Surface reflection and surface scattering are probably the most significant losses at the present time, but ultimately even molecular scattering in the gas that fills the computer could be a limitation.

APPENDIX A
AGENDA
OPTICAL INTERCONNECTS

Materials Research Council
Torrey Pines Elementary School
La Jolla, CA

July 18-19, 1984

WEDNESDAY, July 18

Introductory Remarks	A. Yariv, Cal Tech
DARPA Programs & Future Plans	J. Neff, DARPA
Perspective on Interconnects in Computers	R. Keyes, IBM
Use of Optical Fibers in Banyons	J. Lipovsky, U. Texas
Computer Architecture & Interconnections	H. Brauer, IBM
Chip-to-Chip Interconnect Development at Honeywell	J. Carney, Honeywell
GaAs Wafer Interconnect Development at Rockwell	R. Milano, Rockwell
Direct Optical Addressing of Integrated Circuits	R. Jain, Hughes

THURSDAY, July 19

Ultra High Speed & Integrated Semi- conductor Lasers	K. Lau, ORTEL
Ultra High Speed Detectors & High Speed Considerations	D. Bloom, Stanford
Ultra High Speed Optical Transmission - System & Component Consideration	H. Blauvelt, Hughes
Optical Interconnect Component Development at Lincoln Laboratory	F. Leonberger MIT, Lincoln Lab.
Optically Tuned Gratings for Interconnects	G. Stegemen, U Ariz.
Dynamically Programmable Optical Interconnects: Potential Material Considerations	A. Tanguay, USC
Discussion	

APPENDIX B

ATTENDEES

Optical Interconnects
July 18-19, 1984

NAME	AFFILIATION	PHONE NO.
Ronald Gutmann	RPI/MRC	(518)266-6794
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INTERCONNECTIONS AND VLSI

D. K. Ferry

It is generally felt that large scale integrations of semiconductor devices will eventually entail large numbers of interconnection pin-outs at the periphery of the chip. This fact has led to a number of studies, which invariably give the results in terms of a relationship, that has come to be known as Rent's Rule. Empirically, this relationship gives the number of pins, for a given size module, in terms of a power law relation of the number of gates (or the number of effective blocks) in the module. Validity of this relationship is based upon a number of studies of possible interconnections of present gate arrays, or of experimental results on master slice chips. These latter chips are arrays of devices, whose architectural interconnection is defined by a final mask structure. Consequently, these chips have come to be known as gate arrays.

Gate arrays have found extensive application in the large computer arena for two reasons. Primarily, they entail small number of gates, which can be very fast logic such as emitter-coupled logic (ECL), which are not constrained by chip power considerations. Secondly, large numbers of gate arrays, individually programmed to a particular task, can be fabricated very economically, thus saving cost, although these chips are seldom the limiting cost of the overall computer itself.

The significance of Rent's rule lies not so much in the number of pins predicted for a given size chip, but in the effect it has on the average interconnection length on the chip itself. Chips with an exponent >0.5 generally are found to have long interconnections as a rule, while chips with an exponent <0.5 have an interconnection length (in terms of circuit pitches)

that is independent of the overall number of gates. This has a particular importance in deciding whether on-chip optical interconnections can be expected to become important.

Rent's Rule in VLSI

Early studies of arrays of gates showed that the IBM 1400 computers, 360 computers, and later structures generally obeyed the empirical relationship

$$P = KB^{2/3} \quad (1)$$

where P is the number of pins and B is the number of blocks. More recent studies by Landman and Russo¹ and by Chiba² gave a similar relation in simulations of logic arrangements. However, as the number of gates has grown, it has become more appropriate to list the relation in terms of the number of gates rather than the number of blocks. This becomes

$$P = CG^p, \quad (2)$$

where G is the number of gates on the chip. In Fig. 1, we show the results of these latter groups of authors. In general, their data can be fit with $p = 0.55 \pm 0.06$ and $C = 5.3 \pm 1.2$. However, it was particularly evident in the work of Landman and Russo that some chips began to show a different relationship when the number of gates on a chip became large. More recent studies by Gilbert³ indicated that 100,000 gates could be configured in a manner that gave a much smaller exponent in Eq. (2).

Indeed, it has generally been the experience in very-large-scale integration (VLSI), that the number of pins is much smaller than expected in

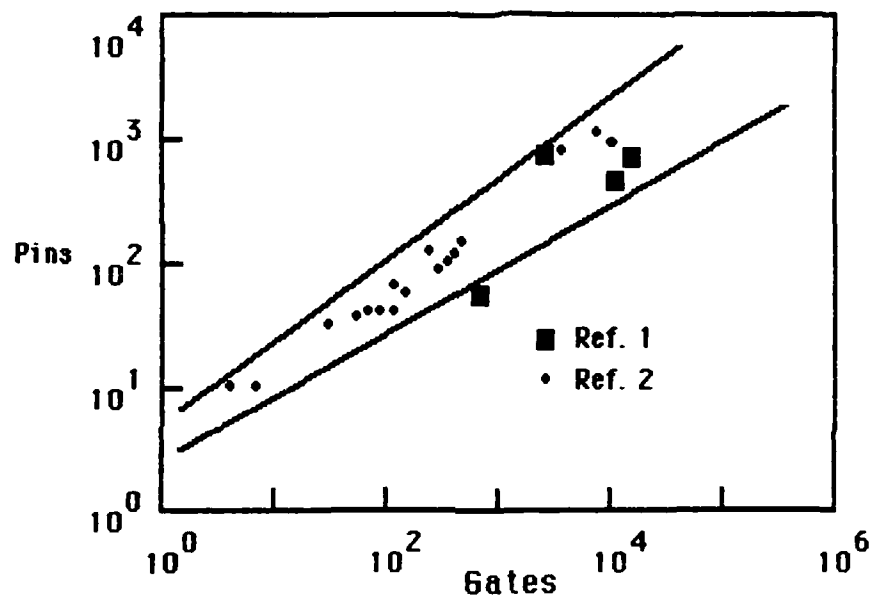


Figure 1. The empirical relationship between the number of pins and the number of gates found for gate arrays. The data is from Refs. 1 and 2.

Rent's rule, at least in terms of the exponents found in gate arrays. However, there has not been to date any careful determination as to whether Rent's rule is satisfied, and as to whether the exponents involved are significantly modified.

In Fig. 2, the results reported for a large number of Si and GaAs LSI and VLSI chips are shown. These points include microprocessors, memories, multipliers, multiplexers, and some GaAs gate arrays. Only the gate arrays differ from the overall trend, and these turn out to fit the earlier version of Rent's rule. From Fig. 2, the best fit to the pin-out of these circuits is found to be

$$P = 76^{0.21} \quad (3)$$

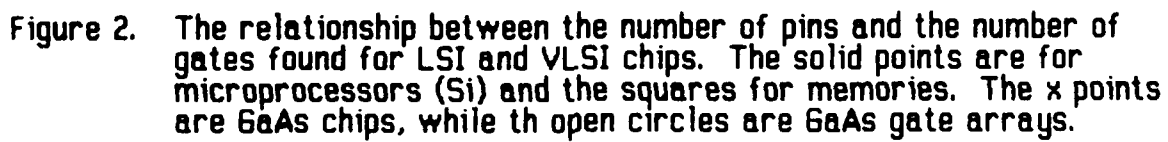
which is significantly different from that found earlier.

Average Interconnection Length

Estimating the average interconnection length on an integrated circuit chip has been an active area of investigation. Modern VLSI circuitry is quite regular in layout, and approximates a square array, which is the system studied carefully by Donath⁴. His results indicate that for an exponent greater than 0.5, the average interconnection length is

$$\langle R \rangle = 6^m \quad (4)$$

where $m = p - 0.5$. For 100,000 gates, this gives an average interconnection length of about 2000 circuit pitches. For comparison, Keyes⁵ reported that a 5000 gate array at IBM was found to contain 5.8m of wire, which indicates some 1mm of wire for each gate. Indeed, the general results found in gate



arrays is that they are very interconnection intensive, with the overall speed limited by the interconnections themselves rather than by the devices^{6,7}. On the other hand, these same authors found that for $p < 0.5$, the average interconnection length is given by

$$\langle R \rangle = f(p) \quad (5)$$

where $f(p)$ is independent of G . For $p = 0.21$, it is found that $\langle R \rangle = 2.9$, which is a three order-of-magnitude reduction in effective length. As a comparison, Hewlett-Packard's 32 bit microprocessor has some 0.25M gates (estimated) and about 7m of wire. This gives about 28 microns of interconnection length per gate. Since the chip is only 0.5cm^2 , the average cell side is only 14 micron. Thus, the average interconnection length seem to be, at least in this chip, about 2 circuit pitches. Still, this is a significant reduction over the IBM results reported above, for a chip that contains significantly more gates.

Impact on Optical Interconnects

It is imperative in any new technology to estimate the impact that this technology will have on future systems. However, the speed of increase of density on VLSI chips is so dramatic that one must be aware of directions being pursued by the semiconductor industry. This is particularly true in the area of impact on advanced computer technology.

Current supercomputers, as well as top-end machines such as the IBM 308X family, do not utilize VLSI chips. The major reason for this lies in the economics of producing a small number of special processor chips whereas gate arrays produced in large numbers can be specialized for each

task. Secondary to this, but still of considerable importance, is the fact that VLSI chips are significantly slower than their gate array counterparts today. For example, the 308X family has a clock spread of 30-50 MHz, while Cray I has a clock speed of 80 MHz. Indeed, the new Cray II is expected to have a clock speed of some 200 MHz. However, there are reasons to expect that gate arrays will have great difficulties in achieving this latter speed at today's 5 V signal levels^{6,7}. VLSI chips on the other hand are somewhat slower. Current 32 bit micro-processors have clock speeds of 10-20 MHz. These speeds are increasing dramatically, however, and VHSIC chips are expected to achieve 100 MHz clock speeds. At the time this is achieved, there will not be a significant speed advantage to gate arrays relative to microprocessors. Consequently, we can expect that these VLSI chips will begin to make significant inroads into super-computer architecture. This will be more prevalent in distributed architectures, where large numbers of equivalent local processors are to interconnected.

VLSI circuitry, as discussed above, is found to have very short average interconnection lengths. Consequently, the dense packing achieved in these chips and the short lengths of the wiring argues strongly against any possible impact of using optical interconnections within a single chip. On the other hand, the large amounts of data flowing from the chip, and to other chips in a distributed architecture, argues strongly for optical interconnection technology. This will probably be especially true in the GaAs chips, currently being developed by DARPA, because of the relative ease of incorporating light sources on the same chip. GaAs off-chip drivers have been demonstrated to achieve a rise time of 0.1 nsec³, but at a cost of 2-3 mW of power. Low threshold quantum well lasers have been demonstrated⁸

with this same power level, and these have the capability for much higher data rates.

The higher data rate expected from integrated lasers is significant for the achievement of truly high capability in future super-computers. A current generation 32 bit microprocessor, running at 18 MHz, generates an effective memory data rate of 0.58 Gbit/sec. Thus, bit-serial data lines are not expected to be effective, even with optical links. However, super-computer designers would like to have the memory band-width some three or more times larger than the processor clock speed⁹. GaAs promises this possibility especially with optical links running bit-parallel.

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COMMENTS ON OPTICAL INTERCONNECTS

R. M. Osgood

In what follows I give my general impression of the optical interconnect work after seeing the program scope and hearing its rationale for the first time:

1) Overall the program has a very strong effect in device development. The work on high speed transmitters, receivers, multiplexers, and modulators seems particularly good. The justification of the program came out less clearly, but after listening to many of the computer engineers it became obvious that high data-rate optical links can be a major advance in computer board to board and box to box communication. Fred Leonberger's viewgraph of the wire-choked back plane of the Cyber computer was very convincing.

2) With only a small leap of faith, it is probably a good assumption that certain chip designs which are "interconnect" intensive, will require optical interconnects. At this point, the DARPA program would benefit greatly by specifically indentifying a narrow class or particular chip where optical interconnects are a sine qua non.

3) In the area of devices, it is clear that advances in fabrication technology oriented toward optical/electrical devices can play a decisive role in expanding our ideas about what devices can be built and even what devices can be envisioned. The work on the window laser and the InP vapor-phase transport for shaping micromirrors showed that clearly. In addition, the use of strained layer epitaxy for growing GaAs over silicon is clearly essential for mixing GaAs and silicon devices on a single chip.

4) As mentioned above the existing device work is impressive, it should be expanded. However, the absence of an experimentally realized programmable grating concept, demands experimental work in this area and is very clearly a priority goal.

OPTICAL INTERCONNECTS

R. Gutmann

Optical interconnect technology has the possibility of contributing significantly to future computer systems. This meeting was extremely useful in obtaining a perspective on the status of the technology and future system needs.

Future computer systems include general purpose machines, supercomputers, special purpose signal processors, microprocessors and symbolic processors. The interconnect requirements differ but will remain severe in large (i.e., multiple chip processors containing densely packed electronic circuitry) processors. Key factors in the interconnect issue include the following :

- distance between interconnections
- delay/link rate requirements
- serial/parallel nature of the signals.

The distance between interconnections is usually defined by the type of interconnection, that is:

- board-to-board (~ .1 to 1.0 m)
- chip-to-chip (~ .01 to 0.1 m)
- within a chip or wafer (1 .00 to .01 m).

As one proceeds from the "board-to-board" towards the "within a chip or wafer" level the spatial density of interconnections increases tremendously. Moreover, the compatibility requirements with electronic chip design increases significantly as well, particularly if there is to be an evolutionary path for optical interconnect technology.

Board-to-Board

Board-to-board interconnect requirements can be easily supplied by optoelectronic technology as monolithic integration with electronic circuitry is not required and size-power-heat constraints are not overly stringent. Optical transceivers with guided or unguided transmission will be most desirable in applications requiring:

- high bit rate transmission
- relatively long interconnect paths
- high density of interconnects
- serial data

Prime examples include interconnection between different memory technologies, between cache and local memory and between memory and logic I/O. While implementation is system specific, it would appear desirable to search for a present computer system that could be improved with an optical transceiver interconnect and proceed to implement such a retrofit. Some optical interconnect demonstration appears desirable in the near term. Another issue raised in the meeting was the pin extensive nature of extendable large scale processors using switching networks based upon banyon topography. Since many such machines are in the demonstration stage, optical interconnect technology might be demonstrated in such a program.

Chip-to-Chip

Chip-to-chip interconnects will be a critical evolutionary step in optical interconnect technology. Compatibility with electronic circuitry (size, power, heat, package) is critical even with more near term hybrid implementation (and of course even more significant when monolithic implementation is considered). Technology programs at Honeywell, Rockwell

and Lincoln Laboratories will demonstrate the capabilities of optoelectronic technology and indicate areas requiring additional research (such as selective epitaxy, low-threshold short-cavity side illuminating lasers and compatible electronic/optoelectronic packaging schemes).

The acceptance of chip-to-chip optical interconnects would depend upon the architecture of the computer. For example, clustering of conventional electronic chips near an optoelectronic chip compatible with fine-grain, distributed layout machines. In fact the availability of such interconnect technology could be paramount to the success of such architectures.

It is crucial that chip-to-chip interconnect feasibility be explored/demonstrated with a suitable computer architecture and electronic design technology. The selection of such a demonstration vehicle may not be straightforward.

Within a Chip or Wafer

The within a chip or wafer interconnect level is quite technically aggressive, more long range and needs further delineation. Since monolithic integration is required, electronics/photronics monolithic compatibility development will require a large funding expenditure. Reconfigurability is an exciting prospect that offers architectural possibilities. However, the advantages need to be delineated with more precision to justify the high-risk technology required.

The advantages of fixed on-chip or on-wafer interconnects are probably not sufficient to warrant such a technology development. Mutual interference and electromigration will probably not be limiting in VLSI scaling to smaller dimensions, while loading capacitance and the drive power length dependence could be alleviated by using L-C lines (instead of R-C lines) on chip.

Near term support should focus on critical materials and device technologies. Besides selective epitaxy, side-illuminating lasers, and electronic photonic packaging as needed for chip-to-chip interconnects, research is needed in reconfigurable technique technologies such as photo-refractive materials, non-linear optics and compatible optical storage (holographic) techniques. Most important architectural designs are needed to guide the materials/device research are to provide the overall technological base required.

WORKSHOP ON FRACTURE TOUGHNESS OF ADVANCED FIBROUS COMPOSITES

A. Argon, B. Budiansky, A. G. Evans and J. W. Hutchinson

INTRODUCTION

This workshop was held as an outgrowth of the 1983 MRC discussions on metal- and ceramic-matrix composites, during which the assessment, understanding, and improvement of fracture toughness were identified as essential problems for further study. The 1984 workshop was structured to include consideration of resin-matrix composites as well, in order to reveal possible areas of relevant technological overlap in the behavior of the various types of fibrous composites. The meeting program and list of participants are included at the end of this workshop report.

OVERVIEWS (Budiansky)

Following a brief introduction to the theme of the meeting by S. Wax (DARPA), overviews were presented by S. Sternstein (RPI), A. Argon (MIT), and A. Kelly (Surrey), on resin-, metal-, and ceramic-matrix fibrous composites, respectively. Sternstein surveyed the use of small-amplitude measurements of dynamic, complex viscoelastic stiffnesses as a tool for material characterization. Various parameters of the fabrication process and their consequent influence on internal stress and composition were shown to have important effects on both in-phase and out-of-phase components of stiffness. Moisture degradation was also studied using this method and shown to be sensitive to the polymer material. The implication that toughness changes could be diagnosed by such non-destructive dynamic

tests, awaits quantitative establishment. Some important affects of fibers on matrix toughness were also described.

Argon contemplated the general problem of how ductile metal matrices reinforced by brittle fibers could be expected to deform and fracture. On the basis of elementary models, Argon discussed the fundamentals of deformation resistance, taking into account plastic matrix deformation and discontinuous fiber effects. Fracture energy was similarly studied, including consideration of fiber pullout and matrix rupture by crater formation, with results that suggest increased toughness for larger fiber diameter. The role of fiber-matrix interface strength in controlling crack paths was examined on a stress basis, and an estimate was made of the highest interface strength that would permit cracks to run along fibers rather than through them.

Kelly discussed the fracture of brittle-matrix, strong fiber composites, and focussed on the "first cracking" problem, in which the matrix cracks while the fibers remain intact. The Aveston-Cooper-Kelly (ACK) theory provides an estimate of this matrix cracking stress, when frictional slip occurs along the interfaces of fibers adjacent to the crack faces. Experiments show that the ACK result provides a lower bound to observed cracking stresses, at fiber volume fractions below 25%.

METAL AND RESIN MATRIX COMPOSITES (Argon)

- A. Damage Accumulation in Unidirectional Composites by S. Batdorf of UCLA. The discussion was directed to the statistics of spreading of a damage zone laterally by the sequential failure of fibers until final

instability. The results were limited by a lack of adequate information on the nature of stress elevation in the surrounding of failed fiber cluster but indicated the importance of decoupling fibers from their surroundings.

B. Fracture Toughness Testing for Interlaminar and Transverse Failures

in Resin Matrix Composites by W. Elber of Nasa-Langley. The presentation covered a wide range of resin matrix components with graphite fibers. Particular emphasis was placed on delamination toughness tests and the relative roles of mode I and mode II in delamination failure. It was thereby demonstrated that the relative contribution of mode I and mode II to failure varied with the matrix toughness. Specifically, the higher the toughness, the greater the influence of mode II. The influence of matrix toughness as cyclic delamination growth rate was also described and it was demonstrated that the threshold diminished as the matrix toughness increased. Finally, a discussion of impact induced damage and delamination was presented.

C. Fiber Stress Concentrations in Boron/Aluminum and Kevlar/Epoxy Monolayers by D. Reedy of Sandia. The presentation covered the results of experiments carried on monolayers of composite consisting of a single row of fibers in a matrix layer responding to cracks of various initial lengths. The stress concentrations obtained by finite element calculations were found to be in very good agreement with those obtained with shear lag analyses. As expected, a reduction in stress concentration was noted in instances where the matrix did not

undergo much strain hardening. Further improvements were found when fibers were allowed to debond.

- D. Fracture Resistance of 2XXX Al/SiC Materials by D. Chellman of Lockheed, Calif. The discussion covered the behavior of a series of precipitation hardened series 2000 aluminum alloys incorporating both SiC fibers and whiskers. Small changes in toughness were achieved with Zr additions.
- E. Interfaces and Fracture in Metal Matrix Composites by H. Marcus, U. Texas. A detailed presentation was given on the measurement of the chemistry, structure and cohesive properties of interface layers between Al matrices and SiC fibers having undergone partial reaction. The measurement of composition gradients across the interface obtained by Auger spectroscopy with systematic sputtering and measurement of residual stresses by x-ray techniques gave a good demonstration of the power of advanced analytical techniques to determine the progress of interface reactions.
- F. Tailoring Interfaces in Metal Matrix Composites by J. Cornie of MIT. The presentation was on the development of sacrificial layers on SiC fibers with interfaces having tailored cohesive properties to protect the fibers from reaction layer damage, and also to permit crack arrest. Both previous preliminary results and plans for a comprehensive investigation were discussed in some detail.

BRITTLE MATRIX COMPOSITES (Hutchinson)

A series of four papers described the mechanical properties of brittle matrix composites. Prewé summarized data obtained on a range of materials. He compared ceramic matrix systems with resin matrix materials, noted the effects of loading mode on failure and assessed the effects of cyclic loading. In particular, he demonstrated that ceramic matrix systems can exhibit high tensile strength, as well as superior bend strength capabilities, with good high temperature potential. Fatigue effects also seem to be minimal in such composites. The work thus far has focussed on glass ceramic matrices, which can be processed to provide excellent mechanical properties. Other, higher temperature matrices, have yet to be adequately explored.

Budiansky described models of matrix cracking for composites containing either debonded or bonded fibers. For unbonded fiber systems (typical of current glass ceramic matrix composites) an optimal cracking stress was derived from a steady state cracking model. The optimum was shown to occur at a specific difference in volumetric mismatch during fabrication between fiber and matrix, which depended only on the friction coefficient and the fiber volume fraction. This optimum provides a key objective for composite fabrication studies. For systems containing bonded fibers, it was demonstrated that debonding only occurs when the interface debond toughness, G_{Id} , is appreciably smaller than the matrix toughness, G_{Im} . The matrix cracking stress in the debond range was also derived. An optimum cracking stress, based on the strength of the fiber and the debond toughness, was then described.

The mechanical characteristics of brittle matrix fiber composites were described by Marshall. Contrasts between the behavior in tension and bending were demonstrated, and the limited use of bend test property characterization was established. A novel method for measuring the shear resistance of the fiber/matrix interface was described and used to provide results for a glass ceramic/SiC composite. The measured value was consistent with the matrix cracking stress determined on the same material. Hysteresis in the matrix cracking opening was also discussed and used to provide independent estimates of the interface friction and of the residual stresses in the matrix. Finally, the behavior of short cracks was analysed. Such cracks were shown to result in a higher matrix failure stress than long cracks, but only when the crack radius is smaller than a few fiber spacings.

Finally, the shear strength of brittle matrix composites was described by Evans. The mechanism of failure was shown to involve the coalescence of microcrack arrays formed in the matrix between fiber bundles. The matrix microcracks form in mode I in regions of high stress concentration between bundles. The ligament between microcracks then coalesced, due to bending, resulting in a macroscopic mode II instability. Calculation of the critical shear strength, based on the microcrack concept, revealed that the shear strength is enhanced by: good bonding between fiber and matrix, homogeneous fiber packing, small fiber loadings and a high matrix toughness. The former are incompatible with good tensile properties, emphasizing the compromise that must be realized in the design and usage of such materials.

DISCUSSION TOPICS (A. G. Evans)

Fiber/Matrix Bonding

The optimum structural properties of composites are critically dependent on the bonding between the fiber and matrix. The specific bonding requirements depend upon the matrix material and the structures subject to consideration. For polymer matrix composites there was substantial agreement that the base of knowledge is sufficient to allow near-optimal bonding to be specified. (Albeit that, the chemistry considerations pertinent to optimal bonding seem less apparent, and subject to problems of propriety compositions, etc.). Briefly, it was agreed that, for structures in which compressive loads dominate, the maximum feasible bonding should be attained (as determined from transverse fracture G_{IC} tests, e.g. double cantilever beam tests). More typically, however, a bond of intermediate fracture resistance is required to resist various combinations of tensile and shear loads, as manifest in the resistance of the composites to delamination and fiber failure. Experience dictates the specific bond characteristics that provide optimal net structural performance (e.g. impact damage resistance), for a particular fiber/matrix material combination. It remains to express the bond properties as a parameter in mechanics models of damage and failure that can be separately measured and related to performance.

For metal matrix composites, one of the primary concerns that dictates consideration of bonding is the reactivity of the matrix with the fiber. Most useful fiber/matrix combinations are liable to chemical reaction during processing, resulting in an interlayer which often dominates the mechanical response of the fiber/matrix regions. Consequently, sacrificial fiber coatings emerge as a requirement for optimal mechanical performance. Acceptance of the coating principle places emphasis on the

interface between the coating and the fiber and/or on the reaction product interface with the matrix or coating. It was agreed that these interfaces must be moderately susceptible to Mode I failure, such that the interface fails in preference to the fiber, in the presence of a coating or reaction product crack. Hence, a measure of the bonding characteristic suitable for good composite properties might be based on tests of individual coated fibers, to ascertain whether initial cracking (subject to tensile loading) occurs preferentially along the interface or across the fiber. Systems which give fiber failure would be undesirable because poor tensile properties would ensue. Low resistance to interface failure would also be unacceptable because of the susceptibility of the composite to transverse (or shear) failure. Some intermediate performance would be optimal, as governed either by an experience base similar to that in polymer matrix systems or by comprehensive mechanics models of axial and transverse failure. For ceramic (or other brittle) matrix composites, the bonding issue is relatively well-defined. Very weak bonding (small ratio of the debond resistance G_{Id} to the matrix fracture resistance, G_{Im} ,) is needed to achieve tensile properties that take advantage of the fibers (Fig. 1), i.e. load bearing capacity beyond the matrix cracking stress. Yet, some bonding is desirable for good shear strength. Covalent bonding at the interface would be totally unacceptable. However, Van der Waals bonding at an interfacial layer would, perhaps, provide the requisites, small value of the ratio, G_{Id}/G_{Im} . Such bonding may be feasible with a surface layer of graphite or with this a thin amorphous oxide layer (Marcus). Studies of interface failure resistance using transverse G_{Ic} tests are needed to examine this issue. Alternatively, bonding can be prevented by an inert interlayer and the

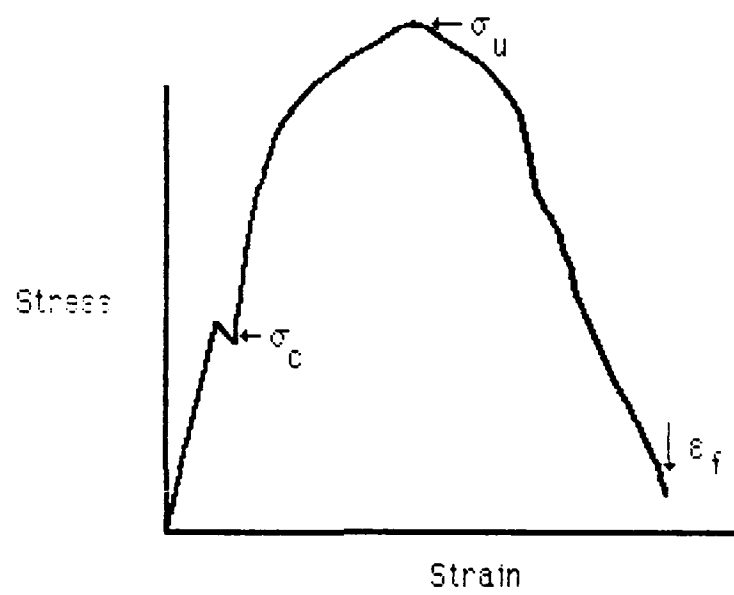


Figure 1.

protection optimized by adjusting the thermal expansion coefficients to give the maximum acceptable interface shear strength, due to frictional slipping against the residual interface pressure (Budiansky).

Fracture Properties for Design

The mechanical properties of a composite that relate to structural performance depend both on the matrix and on the structure. The relevant properties for the most commonly envisioned application for the different composites were discussed.

For brittle matrix composites, applications frequently involve the use of two - or three - dimensional woven reinforcement materials, subject to tensile and shear loads. Tensile loads result in matrix cracking, followed by fiber failure (Fig. 1). Such failure cannot be uniquely characterized either by a fracture toughness (K_{IC} or J_{IC}) or by a work of fracture. Such tests are thus of little utility. The important tensile characteristics are: a high matrix cracking strength (σ_m^C), an ultimate strength (σ_U) in excess of σ_m^C - to ensure load bearing capability after matrix cracking - and a large failure strain, ϵ_f , to resist fragmentation during overstrain transients. The former property can be measured from tensile or bending tests, while the latter properties require tensile tests. Tensile data are thus of prime importance for design purposes. Shear strength data are also required because shear strength are typically much less than the tensile matrix cracking strength. Such strength can be measured using flexural tests.

Recent metal matrix composites are most susceptible to tensile failure, due to a low fracture toughness. Standard J_{IC} and J_R tests should thus be adequate for design purposes, provided that both axial and transverse measurements are made.

Polymer matrix composites are usually used as laminated plates and degrade by delamination or compressive kinking. Delamination toughnesses are then of major interest, as well as compressive kink strengths. The delamination process frequently occurs in mixed mode. Hence, both Mode I, G_{IC} , and Mode II, G_{IIC} , toughnesses are required, in addition to general mixed mode failure criteria. Various Mode I, Mode II and mixed mode tests are thus needed to fully characterize delamination failure and hence, to select optimum matrices for laminated composites.

Matrix Properties

Processing techniques for metal and ceramic matrix composites often result in matrices with different properties than the matrix material, without fibers, made under nominally similar conditions. It was agreed that matrix properties must be measured, in situ, to ensure that the role of the matrix in mechanical strength is adequately described. One good example is the influence of fibers on the toughness of polymer matrices (especially when shear bands are toughness determining entities). Another possible example is the role of fibers as hole nuclei in metal matrix composites and the resultant reduction in matrix ductility and toughness, due to shear band instabilities.

Model Materials

A brief discussion of the role of experiments on model material systems revealed that certain effects could be most systematically studied with such systems. For example, effects of matrix yield strength and thermal expansion coefficient on the fracture toughness of metal matrix composites could be logically investigated and compared with predictions from mechanical models. Research on model systems was thus encouraged.

FRACTURE TOUGHNESS OF ADVANCED FIBROUS COMPOSITES

July 19 & 20, 1984

Thursday, July 19

CHAIRMAN - B. BUDIAISKY

S. Wax, DARPA	Introduction
S. Sternstein, RPI	Resin Matrix Composites, Overview (R)
Discussion	
A. Argon, MIT	Metal Matrix Composites, Overview (M)
Discussion	
A. Kelly, Surrey	Ceramic Matrix Composites, Overview (C)
Discussion	

CHAIRMAN - A. ARGON

S. B. Batdorf, UCLA	Damage Accumulation in Unidirectional Composites (R)
W. Elber, NASA-Langley	Fracture Toughness Testing for Interlaminar & Transverse Failures in Resin Matrix Composites (R)
D. Reedy, Sandia	Fiber Stress Concentrations in Boron/Aluminum & Kevlar/Epoxy Monolayers. (RM)
D. J. Chellman (M) Lockheed-Calif.	Fracture Resistance of 2XXX Al/SiC Materials
H. L. Marcus, Texas	Interfaces & Fracture in Metal Matrix Composites (M)
J. A. Cornie, MIT	Tailoring Interfaces in Metal Matrix Composites (M)
	Discussion

Friday, July 20

CHAIRMAN - J. HUTCHINSON

K. M. Prewé, United Technologies	Observations of Fracture in Metal Matrix & Ceramic Matrix Composites	(MC)
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B. Budiansky, Harvard	Analysis of Matrix Cracking in Brittle-Matrix Fibrous Composites	(C)
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D. Marshall, Rockwell	Matrix Cracking in Ceramic- Matrix Composites	(C)
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A. G. Evans, Berkeley	Shear Model of Failure in Ceramic Matrix Composites	(C)
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Others - Discussion

CHAIRMAN - A. G. EVANS

Discussion & Recommendations

R = Resin

M = Metal

C = Ceramic

ATTENDEES FRACTURE TOUGHNESS OF ADVANCED FIBROUS COMPOSITES

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METAL MATRIX COMPOSITES

A. S. Argon

INTRODUCTION

The general review, the specific contributions, and the following general discussion concentrated on a number of key problems affecting the performance of metal matrix composites. Although the principles of reinforcement of metals with fibers are not very different from those in resin matrixes and ceramic matrixes, the more ductile behavior of metals under relatively slowly increasing plastic resistances influences the nature of coupling between fibers and the eventual mechanisms of fracture. In addition, the interfacial reactions between matrixes and non-metallic fibers are usually much stronger in metal matrix composites requiring special recognition and special procedures for their control. We will discuss below first the general principles and specific conclusions that were clarified by the workshop discussions, and then present a short summary of the contributions of individual participants.

KEY PHENOMENA IN METAL MATRIX COMPOSITES

Axial Deformation Resistance of Composite with Aligned Fibers

In a composite with continuous fibers no fracture should occur at strains less than σ_f^*/E_f where σ_f^* and E_f are the fracture stress and Young's modulus of the fibers. Thus, as long as the strength of the fibers do not degrade in time the composite with a volume fraction V_f of fibers will support a stress, $\sigma_c < \sigma_f^* V_f$ for long periods of time. Since fiber fractures occur, however, in handling and processing into a composite, it is more realistic to plan for a performance that is limited by discontinuous fibers

with a given aspect ration of l/d .

An analysis of Street (1971) gives that the deformation resistance of such a composite is in the limit of ideal plastic behavior of the matrix:

$$\sigma_c = (\sigma_f^* v_f / 2) + \sigma_m (1 - v_f) \quad (1)$$

where σ_m is the average plastic resistance in tension of the metal matrix. Since σ_f^* / σ_m is usually 10-20 for composites utilizing strong non-metallic fibers in ductile metals.

$$\sigma_c = v_f^* v_f / 2 \equiv \sigma_{th} \quad (2)$$

This can be taken as a threshold strength where the composite exhibits yield-like behavior after all fibers undergo a fragmentation process to a critical aspect ratio of

$$l_L / d = (3.05/2)(\sigma_f^2 / \sigma_m) \quad (3)$$

Modes of Fracture of Aligned Composite

Once the composite exhibits yield-like behavior with fragmented fibers it will undergo fracture in two limiting modes.

If the initial fragmentation of the fibers had been quasi-homogenous with the fiber fractures showing no spatial correlation as indicated in Fig. 1. The work per unit area $x_{pull-out}$ to separate the composite along any specific plane is roughly

$$x_{po} = \sigma_{th} \cdot W \quad (4)$$

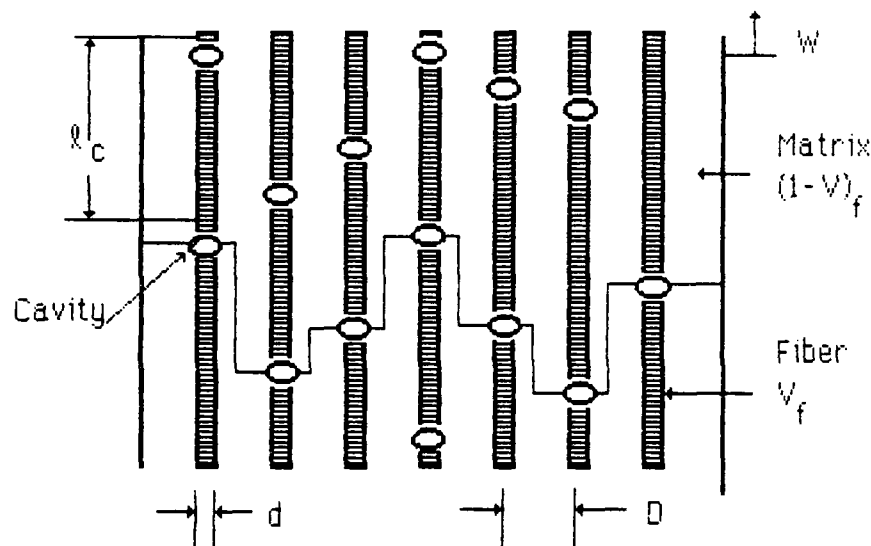


Figure 1: Schematic view of composite with uncorrelated fractures, showing a possible separation surface requiring fiber pull-out.

Where the separation distance W depends on the limiting strain to fracture E_{mf} that the matrix can sustain, i.e.,

$$W \approx 3^{0.5}(D-d)\epsilon_{mf} \quad (5)$$

$$x_{po} = 3^{0.5}v_f(1-v_f^{0.5})\sigma_f^*D\epsilon_{mf} \quad (6)$$

The expression in (6) reaches a maximum value of $V_f = (2/3)^2 = 0.44$, for constant interfiber spacing D , fiber strength σ_f^* and matrix strain to fracture E_{mf} ; for which

$$x_{po \max} = 0.128\sigma_f^*D\epsilon_{mf} \quad (7)$$

Y, the fiber fractures are correlated and nearly in a plane, as should be the case for fibers with little variation in strength, coupled tightly by a matrix of high deformation resistance, the eventual separation will involve only the fracture of the metal ligaments between the fractured fibers as indicated in Fig. 2. The work per unit area X_{dimple} to form a collection of close packed dimples is roughly.

$$X_d = 4(1-\nu_f^{0.5})^2 D \sigma_m \epsilon_{mf} \quad (8)$$

Where the average strain to failure ϵ_{mf} can reach a limiting value of $(1/(2 \tan \alpha))$ when the metal ligaments rupture with a ridge half angle of α as shown in Fig. 2 giving for $\epsilon_{mf}(\text{max}) \approx 0.5$.

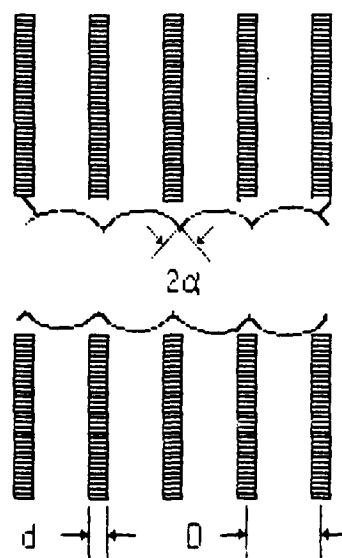


Figure 2. Schematic view of composite with correlated fractures in fibers, showing a nearly planar separation by matrix fracture or rupture.

It is instructive to evaluate the two limiting modes of fracture for a typical case of $\alpha^*_f = 7 \text{ GPa}$ (10^6 psi). $D \approx 10^{-5} \text{ m}$. $E_m/E_f \approx 0.1$, $\nu_f = 0.44$, $\alpha_m = 300 \text{ MPa}$ (aluminum alloy); this gives

$$x_{po} = 900 \text{ J/m}^2 \quad (9a)$$

$$x_d = 162 \text{ J/m}^2 \quad (9b)$$

These two limiting modes give rise to tensile fracture toughness of

$$K_{IC} \approx (2x_{po}E_c)^{0.5} = 21.3 \text{ MPa m}^{0.5} \quad (10a)$$

pull-out

$$K_{IC} \approx (2x_dE_c)^{0.5} = 9.0 \text{ MPa m}^{0.5} \quad (10b)$$

dimple

where

$$E_c = \nu_f E_f + (1-\nu_f)E_m \approx E_f(0.44 + 0.56E_m/E_f)$$

$$E_c = \nu_f E_f + (1-\nu_f)E_m \approx 0.72 E_f$$

for

$$E_m/E_f = 0.5 \text{ and } E_f \approx 350 \text{ GPa } (50 \times 10^6 \text{ psi})$$

Considering that the fracture propagation is initiated when the matrix reaches the threshold stress and exhibits yield-like behavior it is instructive to determine the damage zone diameter R ahead of a macrocrack for these two limiting modes of propagation.

$$R = K_{IC}^2 / \pi \sigma_{th}^2 = 2(3)^{0.5} \pi \nu_f (1-(\nu_f)^{0.5}) \sigma_f^* D E_m/E_f (0.72) / 0.5 \pi \sigma_f^*{}^2 \nu_f^2 \quad (11)$$

pull-out

$$R_{\text{pull-out}} \approx 6D$$

$$R_{\text{dimple}} \approx 16(1-v_f^{0.5})D\sigma_m\epsilon_{mf}(0.72)E_f/\pi\sigma_f^*2v_f^2 \quad (12)$$

$$R = 0.5D$$

Thus, in the correlated planar fracture the composite fails with practically no "plastic" zone ahead of the crack while in the uncorrelated fracture of fibers a "plastic" zone of about 6 fiber spaceup in present.

In summary, the best expected performance of a metal matrix composite of, say an aluminum alloy matrix with $V_f = 0.44$ of SiC fibers is roughly (for $\alpha_f^* = 7 \text{ GPa}$)

$$\sigma_c = \sigma_{th} \approx 1.5 \text{ GPa}$$

$$K_{IC} = 21.3 \text{ MPa m}^{0.5}$$

$$\chi = 900 \text{ J/m}^2$$

Reaching this goal requires de-coupling of fiber fractures. This will be difficult without de-bonding of the fiber from the matrix to avoid local stress concentrations. A way to achieve this which also protects the fibers from degradation by a fiber-matrix reaction will be suggested in the next section.

Controlled De-Bonding of Fibers

A prevalent problem in metal-matrix composites is the fiber-matrix reaction that consumes the fiber at its periphery and commonly results in cracks in the reacted layer that can penetrate into the fiber and result in loss of fiber strength. To protect the fiber from such weakening it is attractive to provide the fiber with a sacrificial coating bonded to the main fiber by a bond of tailored strength.

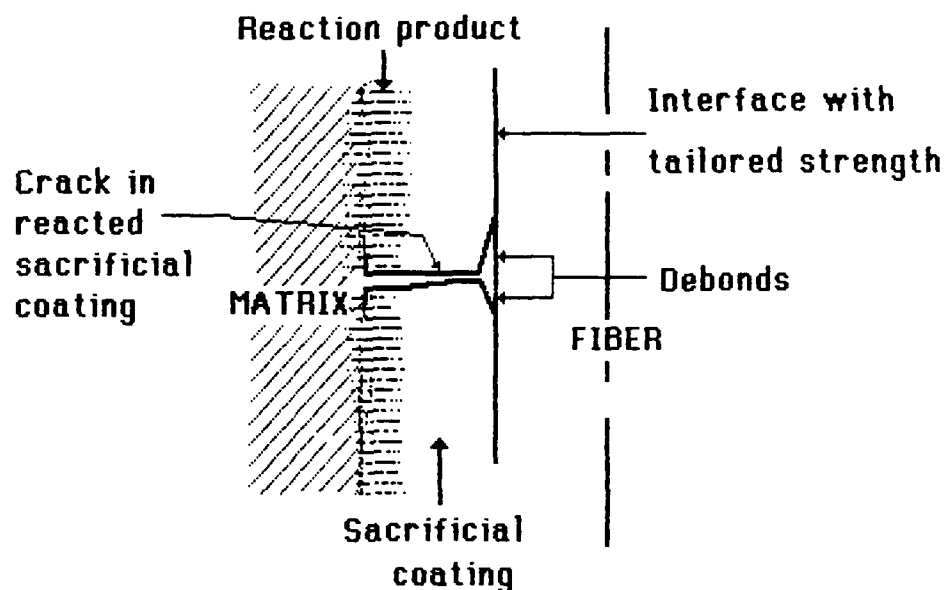


Figure 3. Fiber with sacrificial coating.

As in shown in Fig. 3, an interface with controlled strength can protect the fiber from damage by debonding. Such debonding can also effectively reduce stress concentrations in fibers due to fractures in neighboring fibers and result in a more quasi-homogeneous distribution of primary fiber fractures to permit a toughness performance near the upper limit governed by random fiber pull-out discussed in the preceding section.

Proper Tests to Measure Properties of Composite and Components.

The performance of the composites depends on the properties of fibers and the matrix, and on the strength of the interface.

Although the strength of the fibers, the deformation resistance of the matrix can be measured in isolation or in bulk before the experiment, and the quality of the interface can be studied by microscopy, it is essential to measure these properties in independent tests. Such tests have been

discussed both during the contributed papers session and in the following general discussion. Many tests such as enforced shear parallel to the fibers to measure the shear strength of the matrix; double cantilever test, propagating cracks parallel to the fibers to measure matrix decohesion work and/or fiber debonding work are widely used. More imaginative and special tests to measure other properties in partially idealized model experiments are necessary to determine other properties and phenomena, such as friction between matrix and de-bonded fibers, thermal stresses in the fiber and matrix, chemistry and cohesive properties of reacted interfacial zones. In addition careful examination of fractured specimens to determine the mode of accumulation of damage and partially completed fracture separation processes should prove to be rewarding.

MATRIX CRACKING IN CERAMIC-MATRIX COMPOSITES

B. Budiansky, A. G. Evans, and J. W. Hutchinson

INTRODUCTION

This note summarizes the results of analyses of so-called "first cracking" in brittle matrix composites. The configuration and notation are shown in Fig. 1. Steady-state matrix cracking, in which a long matrix crack is considered to run under a constant critical applied stress, leaving the fibers intact, is illustrated in Fig. 2. Two cases are considered:

(1) unbonded fibers, held in the matrix by a normal initial pressure, q , that resist slip by friction up to a critical shear stress τ , and (2) bonded fibers, that may support an initial interface tension ($q < 0$), but may be debonded by the high stresses near the tip of an advancing matrix crack. As shown in Fig. 2, matrix cracking in either case could conceivably occur without relative displacement between the fibers and the matrix.

FRICTIONAL SLIPPING

For case (1), the Aveston-Cooper-Kelly (ACK) theories developed during the 1970's (see ref. 1 and the references therein) provide results equivalent to the following. For the no-slip case, the composite stress at matrix cracking is

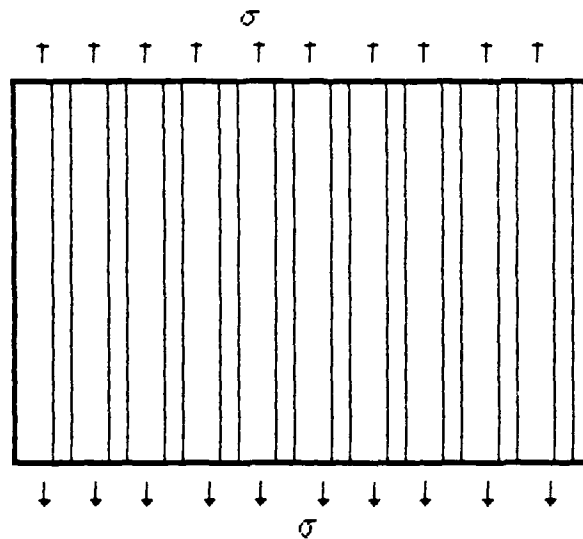
$$\sigma_{cr} = \sigma_0 = \{c_f G_m E E_f \rho / a E_m\}^{1/2} \quad (1)$$

where

$$\rho = \{c_m (E_f/E) (1+\nu_m) \log (1+\sqrt{E_f}/2\sqrt{c_f})\}^{-1/2} \quad (2)$$

MATRIX CRACKING

(intact fibers)



PARAMETERS

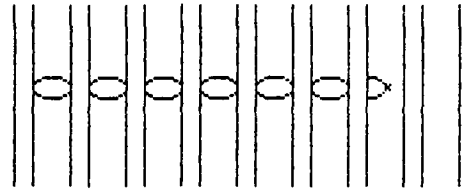
c_f, c_m	fiber, matrix volume fractions
E_f, E_m	fiber, matrix moduli
E	composite modulus, $\cong c_f E_f + c_m E_m$
a	fiber radius
σ	composite stress
σ_m^T	matrix thermal stress
q	interface thermal pressure
τ	interface slipping shear stress
K_m	critical, mode I matrix stress-intensity factor
G_m	critical, mode I energy-release rate
G_d	critical, mode I debonding energy-release rate

FIGURE 1.

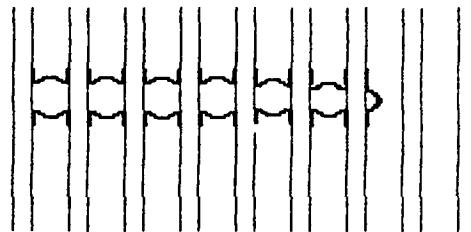
STEADY-STATE MATRIX CRACKING

1. Unbonded Fibers ($q \geq 0$)

a. no slip



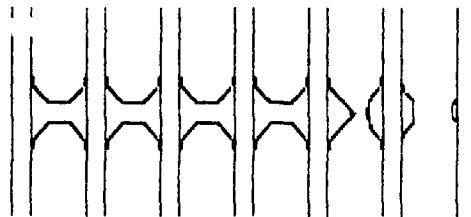
b. slipping fibers



2. Bonded Fibers ($q \neq 0$)

a. no debonding \rightarrow same as 1(a)

b. debonding fibers



crack-tip debonding

FIGURE 2.

and ν_m is the matrix Poisson ratio. (The ACK result actually involves a slightly different definition for ρ .) For large amounts of slip in the wake of the advancing matrix crack

$$\sigma_{cr} = \{(6\pi G_m/a)/(c_f^2 E^2 E_f/c_m E_m^2)\}^{1/3} \quad (3)$$

The present analysis gives, over the full range of the shear-resistance parameter

$$\Gamma = \{4c_f t^2 E a / C_m^2 G_m E_m E_f \rho^3\}^{1/6} \quad (4)$$

The results

$$\sigma_{cr} = \sigma_0 - (E/E_m)\sigma_m^T \quad \text{for } \Gamma \geq 1 \quad (5)$$

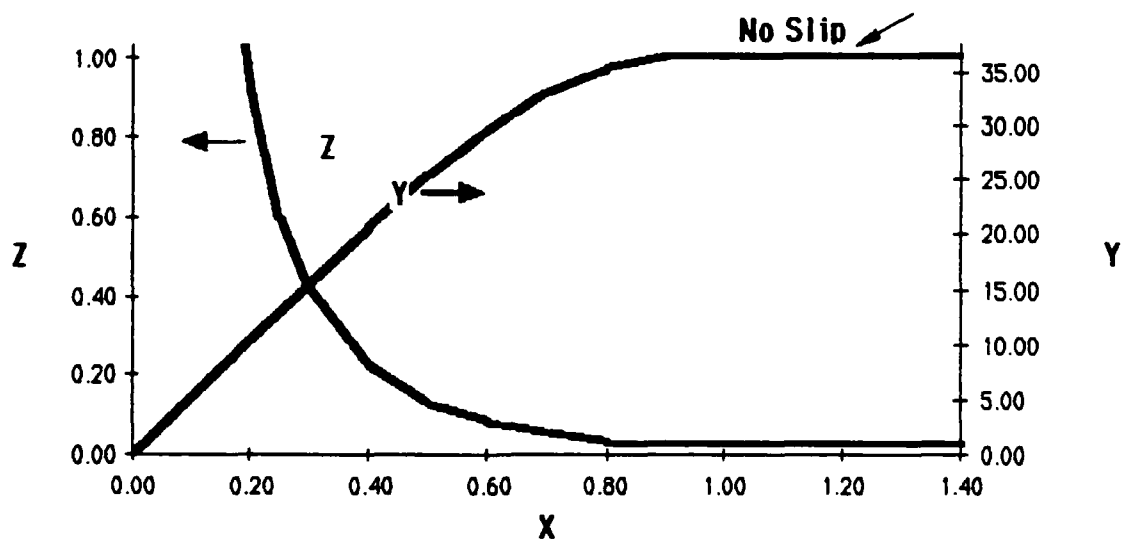
$$\sigma_{cr} = \sigma_0 f(\Gamma) - (E/E_m)\sigma_m^T \quad \text{for } \Gamma \leq 1$$

where the function $f(\Gamma)$ is given parametrically by

$$\Gamma = [3/(\gamma^3 + 3\gamma - 1)]^{1/6} \quad (6)$$

$$f(\Gamma) = \gamma \Gamma^3$$

for $1 \leq \gamma \leq \infty$. Here σ_m^T is the initial, axial thermal (or fabrication) stress in the matrix. Figure 3 shows $(\sigma_{cr} + (E/E_m)\sigma_m^T)/\sigma_0$ versus Γ . For $\Gamma \rightarrow 0$, (6) gives $f(\Gamma) \approx 3^{1/3}\Gamma$ which, via (5), reproduces the large-slip ACK result. The slip lengths l associated with the solution (5) are given by (Fig. 3).



$$X = \Gamma = (4c_f \tau^2 E_a / c_m E_m E_f \rho^3)^{1/6}$$

$$Y = \rho l / a$$

$$Z = (\sigma_{cr} + E/E_m - \sigma_m^T) / \sigma_0$$

FIGURE 3.

$$\rho l / a = (\tilde{\sigma} / \sigma_0) \Gamma^{-3-1} \quad (7)$$

where $\tilde{\sigma} = \sigma_{cr} + (E/E_m) \sigma_m^T$. For $\Gamma \rightarrow 0$, this gives the limiting ACK result

$$l/a = (\tilde{\sigma} / 2\tau) (c_m E_m / c_f E) \quad (8)$$

Finally, Fig. 4 illustrates the variation of ρ with c_f and E_f/E_m .

INITIAL MISMATCH STRESSES

Assuming isotropic fibers and matrix, the initial stresses in the composite can be estimated by

$$q = A_1 \{ c_m E_m / 2(1-\nu) \} \Omega \quad (9)$$

$$\sigma_m^T = A_1 \{ E_m / 1-\nu \} \Omega$$

where Ω is the mismatch strain during fabrication, defined by $\Omega \equiv$ (matrix compressive strain - fiber compressive strain) and ν is Poisson's ratio, assumed to be the same for fiber and matrix. (Note that Ω may not be simply calculable on the basis of temperature changes and thermal expansion coefficient, since effects such as crystallization volume changes and creep may affect Ω . The quantities A_1 and A_2 are given by

$$A_1 = (1-\nu^2)/\Delta$$

$$A_2 = ((1-\nu^2)/\Delta)(E_f/E)\{1+(\nu E)/E_f\}-(c_m(1-\nu)/2)(1-(E_m/E_f))\} \quad (10)$$

where

$$\Delta = 1-(c_m(1-\nu)/2)(1-E_m/E_f)-\nu^2 E/E_f$$

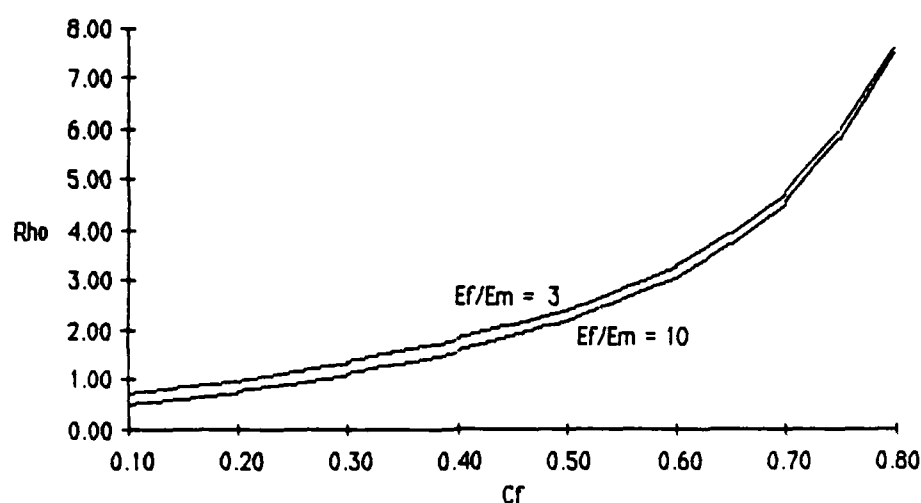


FIGURE 4.

Sample variations of A_1 and A_2 with c_f , for two values of E_f/E_m , are shown in Fig. 5.

UTILITY CONSTANTS

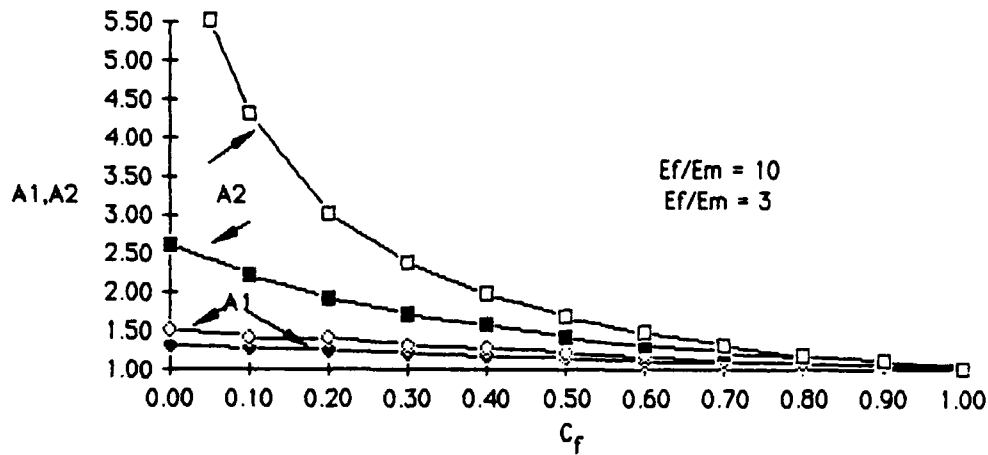


FIGURE 5.

OPTIMAL MISMATCH STRAINS

If $\tau = \mu q$ during slip, where $q > 0$ and μ is a coefficient of friction, it appears from Eq. (5) that an optimum value of Ω may exist for maximizing σ_{cr} , since both τ and σ_m^T increase with increasing Ω . If we presume that the optimum Ω would produce matrix cracking in the large slip range, we can maximize

$$\sigma_{er} = \{(6\mu q G_m / a) \cdot c_f^2 E^2 E_f / c_m E_m^3\}^{1/3} - (E/E_m) \sigma_m^T \quad (11)$$

to get

$$\Omega_{opt} = (c_f(1-\nu)/3) \{ \mu G_m / a E_m \}^{1/2} \{ E_f / E \}^{1/2} \{ A_1 / A_2 \}^{1/2} \quad (12)$$

This gives

$$(\sigma_{cr})_{opt} / E = A_2 \{ 2\Omega_{opt} / (1-\nu) \} \quad (13)$$

or

$$(\sigma_{cr})_{opt} / \sigma_0 = 2/3 \{ C_f \mu / \rho \}^{1/2} \{ A_1 / A_2 \}^{1/2} \quad (14)$$

Also, at the optimum Ω ,

$$\tilde{(\sigma_{cr})} / \sigma_0 = 3/2 (\sigma_{cr})_{opt} / \sigma_0 \quad (15)$$

and so, with plausible values of μ , we find that the optimum would generally occur in the large slip, ACK range (see Fig. 3). This is consistent with the large slip length associated with the maximum σ_{cr} , given by

$$l/a = (3/c_f \mu)(A_2/A_2) \quad (16)$$

It should be mentioned that enough fiber matrix interface roughness could invalidate the assumption of Coulomb sliding, supplying a sliding resistance τ even with $q = 0$ (and unbonded fibers).

BONDED FIBERS; CRACK-TIP DEBONDING

A primitive analysis of the situation shown in Fig. 2 for case (2) supplies the debonding length l_d produced by crack-tip stresses as a function of G_d/G_m , the ratio of mode I debonding and matrix-cracking toughness. For the special case $q = 0$, the result is given parametrically by

$$l_d/a = (1 + \sqrt{c_f}/2\sqrt{c_f})(\sqrt{(1-\nu)/2})X \quad (17)$$

$$G_d/G_m = ((1/128\pi)(1 + \sqrt{c_f})^2/\sqrt{c_f}(1 - \sqrt{c_f}))(\sqrt{2/(1-\nu)})Q(X)$$

for $0 \leq X < \infty$, where

$$Q(X) = \left(\int_0^X (\cosh s ds) / (\sqrt{s} / \cosh x) \right)^2 \quad (18)$$

Figure 6 shows debond length as a function of G_d/G_m for several values of c_f . The upper branches of the multiple valued curves are the

DEBOND LENGTH

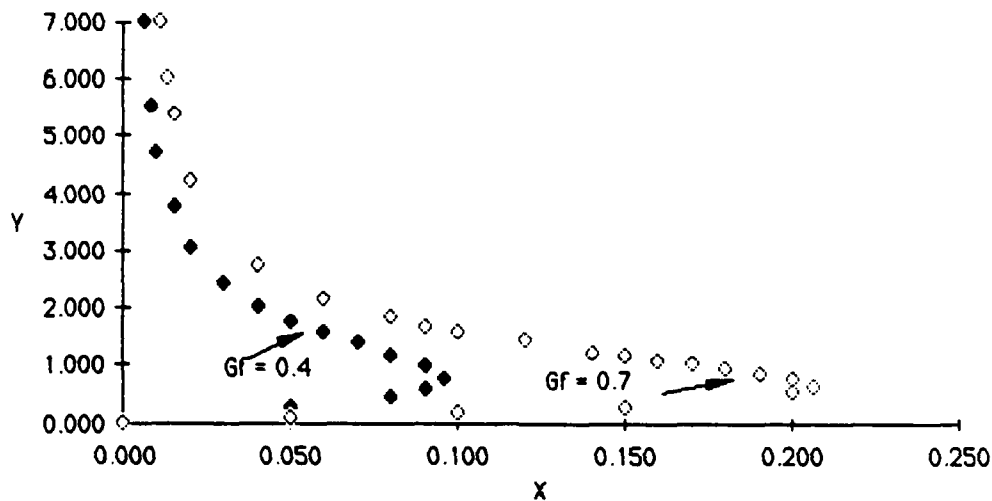


FIGURE 6.

stable ones. The lower branches may be considered to represent barriers to be overcome in order for debonding to occur. (We presume that enough flaws are present to permit this to happen.) Note that for each c_f there is a maximum G_d/G_m above which debonding can not occur. This is shown in Fig. 7, wherein threshold values $(G_d/G_m)^*$ are shown versus c_f .

THRESHOLD BOND TOUGHNESS

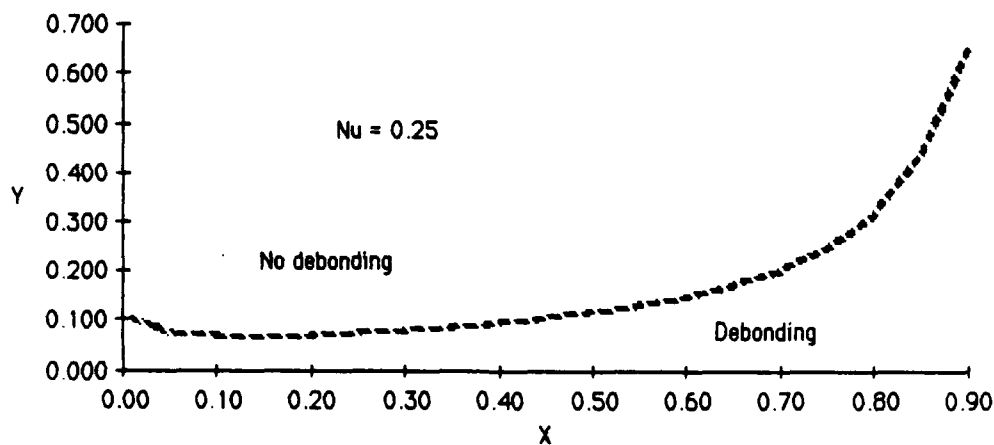


FIGURE 7.

In terms of the values of l_d/a thus found, the matrix cracking stress (again, for $q = \sigma_m^T = 0$) stress has been shown to be given by

$$\sigma_{cr}/\sigma_0 = \{1 + (4c_f/c_m)(l_d/a)(G_d/G_m)/(1 + \rho l_d/a)\}^{1/2} \quad (19)$$

This result is exemplified in Fig. 8 for $c_f = .6$ and $E_f E_m = 3$. Only for rather small values of G_d/G_m will matrix cracking with debonding occur.

A design danger not addressed by the present analysis is that without debonding (or slip, in the friction case) matrix cracks may propagate into the fibers, robbing the composite of the reserve strength and ductility it otherwise could retain beyond matrix cracking.

REFERENCE

1. D. T. Hannant, D. C. Hughes, and A. Kelly, "Toughening of Cermet and Other Brittle Solids with Fiber," Phil. Trans. Am. Soc. Bond., A310, 175-190 (1983).

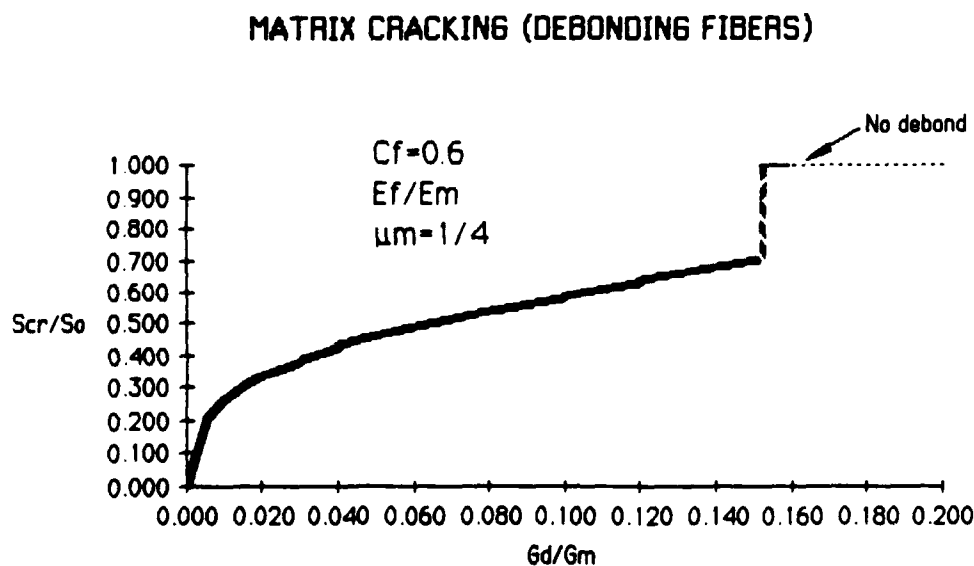


FIGURE 8.

THE SHEAR STRENGTH OF BRITTLE MATRIX FIBER COMPOSITES

A. G. Evans

Brittle matrix fiber composites typically fail in shear at stresses (~ 50 MPa), much less than the tensile matrix cracking stress (~ 300 MPa). The design of composites for optimum shear strength is thus of crucial importance to the practical application of these materials.

Recent observation of shear damage in such composites has revealed matrix microcracks several fiber spacing in length, inclined at $\sim \pi/4$ to the shear stress. These cracks must be induced by stress concentrations. The necessary concentrations are considered to derive from fiber packing inhomogeneities, in the presence of debonded fibers (Fig. 1).

Before eventual shear failure, the microcracks tend to form en echelon, as a damage zone. A crack configuration of this type is susceptible to bending of the intact ligaments (Fig. 1). The bending induces tensile stresses at the ends which cause the cracks to coalesce. Shear failure is considered to occur as a result of this coalescence process, with the intervening matrix being ejected as the failure progresses.

An estimate of the shear strength based on the ligament bending has been made. To obtain this estimate, it is assumed that most of the shear strain is concentrated in the plane of microcracks that produce the final failure. Thus, the strain energy in the ligaments can be regarded as the primary crack driving force. Hence, equating the strain energy to the energy of the new surfaces, a critical displacement for steady state shear failure, Δ_c , is derived as:

$$\Delta_c l = 4\sqrt{2} (K_m/E_m \sqrt{l})(l/E) \quad (1)$$

DAMAGE COALESCENCE

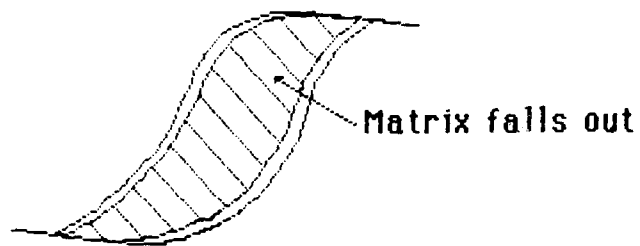
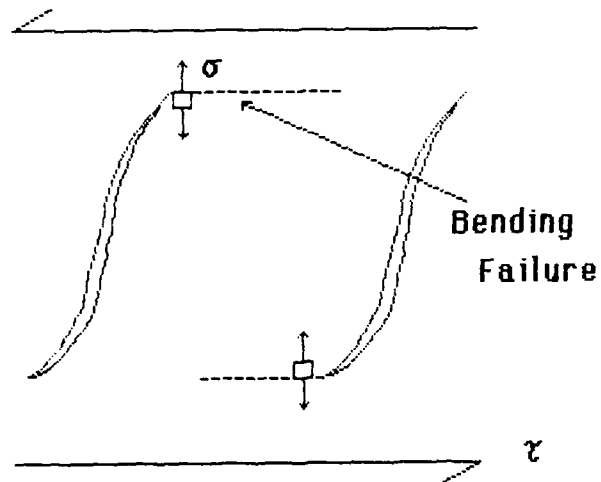


FIGURE 1.

Where K_m is the matrix toughness, E_m is the matrix modulus, l , is the length of the microcracks and t is their spacing. This critical displacement can be re-expressed as a critical imposed shear stress,

$$\tau_c = f^{5/4} K_m / 2(2-f) (1-\nu) \pi^{1/4} \sqrt{a} \quad (2)$$

when f is the volume fraction of fiber and a is the fiber radius.

It is evident from the preceding summary that two of the properties which provide good shear resistance - good fiber/matrix bonding and small fiber concentrations - are incompatible with a good tensile matrix cracking stress (Budiansky). A compromise of tensile and shear properties is thus inevitable. However, it is noted that a high matrix toughness is desirable for both tensile and shear performance.

AD-HOC SESSION ON NEW DIRECTIONS IN METALLURGY

P. Parrish, R. Mehrabian, J. P. Hirth, and J. C. Williams

INTRODUCTION

The major thrust of the DARPA program in metallurgy over the past several years has been rapid solidification technology (RST). RST has served to stimulate the imaginations of the metallurgical community, especially with regard to consideration of new processing techniques for control of microstructural features and subsequent properties at levels down to micrometers with dispersoids of 20 nanometer scale for optimum performance. The potential payoffs for such microstructural control include much greater structural properties, high temperature capability, greater environmental resistance, and novel magnetic and electrical behavior. Within DoD, RST is gaining acceptance and incorporation into research and development plans and road maps to provide higher performance materials for emerging weapons systems applications.

DARPA has nearly completed its mission with respect to RST, with no plans to continue its support past currently supported programs, which end in FY 86/87. Consequently, it was decided that at the MRC Conference, this ad-hoc rump session would be undertaken in order to begin to identify new directions in metallurgy which DARPA (and other agencies) may have an interest in developing in the coming years. The workshop participants included the metallurgists among the MRC members, selected invited participants from both industry and academia and members of DARPA-MSD and DoD services. Due to the short time span in announcing the meeting, a number of desired inputs from others within the metallurgical community were

unavailable, these inputs will be incorporated into this overall process through subsequent meetings within the next few months.

Several general directions emerged from this rump session - they may be broadly described as 1) emerging generic metallurgical research and, 2) emerging new classes of materials:

GENERIC METALLURGICAL RESEARCH

- Small particle, thin film and laminate, and surface metallurgy.
- Opportunities for greatly enhanced properties based upon ultrafine microstructure.
- New metallurgical synthesis/processing techniques based on emerging electromagnetic energy sources, e.g., improved lasers and rail guns, and pressure sources.
- Intelligent materials processing utilizing both improved analytical process models and heuristic models based on artificial intelligence/expert systems concepts for real-time process sensing and feed-forward process control to achieve desired microstructures and properties, (e.g., for processing of very complicated materials such as improved composites, direct consolidation and thermo-mechanical processing of metastable-equilibrium alloys).

EMERGING CLASSES OF MATERIALS

- Multifunctional composites having desired combinations of mechanical magnetic, electrical, etc., properties; tailored, for example, for combined structural integrity, laser hardness and RAM/RAS capability.

- Synthesis and conditioning routes for new metastable equilibrium materials.
- Improved electronic and magnetic materials based on physical metallurgy concepts.
- Foamed metals with high surface/volume for subsequent processing to develop new lightweight structures.
- Gradient and laminated alloys for improved strength resistance to severe, complex environments.

In summary, the sense of this group's activity revolved around the emerging capability for metallurgists to "tailor" or "engineer" metallurgical compositions and microstructures at the micrometer and sub-micrometer scale in order to achieve new materials and performance capabilities based on new synthesis and processing concepts and the possibility of utilizing expert processing to "build in" novel hybrid microstructures. To accomplish this goal, existing models of structure-property relationships must be extended down to dimensions where they currently do not pertain. The successful achievement of this will therefore require the revision of existing models, the development of some new ones and the execution of carefully planned experiments to test the models.

Summaries of the two workshop sessions follow.

MICROSTRUCTURE PROPERTY RELATIONS

A discussion group on this topic was held, with attendees being, A. Argon, J. Hirth, N. Patton, G. Vineyard, B. Wilcox and J. Williams. A number of useful topics were suggested for examination both by theory and experiment. This section summarizes those for which a consensus was reached.

Ultrafine Microstructures

This subject or class of materials has not been thoroughly studied. Yet, as discussed in the DARPA/MRC reports for 1982 and 1983, there are reasons to expect great improvements in properties (strength and toughness in particular) for materials with all microstructural features less than ~20 to 40 μm . There are now a variety of methods which permit fabrication of ultrafine microstructures of this type in a variety of materials. These include:

- Electrodeposition (with and without dispersoids)
- Composites (both laminates and fibers)
- Plasma deposition
- Rapid solidification processing

In addition, there is some evidence that post-fabrication processing of ultrafine microstructure materials can provide additional benefits and microstructural flexibility. This latter point has been demonstrated in Cu-Nb.

Microstructure Scale Effects for Ultrafine Microstructures

The scaling rules for microstructure-property relations in ultrafine microstructure have not been thoroughly examined. Moreover, various properties (e.g., fatigue, toughness, strength) may not scale in the same way in the range of characteristic microstructural features represented in

ultrafine microstructure materials. As a result it appears that better models are needed which will work in size scales where continuum mechanics breakdown. Simultaneously, experiments should be conducted to check these new models and a theory-experiment feedback loop should be established.

Interface Effects

There appears to be a class of problems related to the presence of interfaces which merit theoretical analysis coupled with experiment. These have relevance to composite materials, ultrafine microstructure materials containing rigid particles, and electronic devices. These problems can further be subdivided into interface fracture phenomena and the role of interfaces in deformation, yielding and ductilization. The former problems focus on local fracture criteria for the opening of interfaces and the events leading to this. In particular better estimates of the critical parameters (size, adhesion) influencing decohesion are needed. The latter relate to the role of interfacial structure on initialization of yielding, especially in the case where the material on one side of the interface is normally considered to be non-deforming and brittle.

Brittle Materials - Ordered Matrix Alloys

There is a continuing interest and a renewed need for intermetallic compounds (monolithic ordered phases) for use at elevated temperatures. Among the materials of interest are Ni_2Al , NiAl , Fe_2Al , FeAl , Ti_2Al , and TiAl . Some of the issues which need to be studied, both theoretically and experimentally, in greater detail include the following:

- The relationship between deformation and ductility including the extent to which grain boundary fracture intervenes. It is not yet known whether failure is

associated with a limited number of slip systems to accomodate flow near boundaries or whether adsorbed impurities influence crack initiation and propagation at grain boundaries.

- The role of ternary and higher order solid solution additons on strength, degree of order and deformation character.
- The manipulation of the microstructure of these materials by introduction of whiskers, fibers, dispersoids and other ordered phases.
- Are there other compounds, including those in other crystal systems, which are potentially interesting but are not currently being considered?

Porous Materials

Porous materials offer a number of interesting structure-property opportunities. There is general agreement that porous materials are potentially interesting but additional thought is required to provide focus for a new effort in this area. Ashby's ideas seem promising for systems with large (>50%) porosity volume fraction, but new models seem to be needed for low value fractions.

Electronic and Magnetic Materials

There is a significant body of information regarding defect formation and propagation, solute (impurity) interaction with these defects and precipitation of impurities and excess solutes. Some of this has been successfully applied to electronic and magnetic materials technology but much of it has not. Accordingly, there are real opportunities for

metallurgists trained in microstructure characterization, solidification and structure-property relations to contribute to the understanding of the performance of electronic and magnetic materials. Specific areas of interest include:

- Studies of solute strengthening
- Defect characterization
- Precipitation studies
- Growth defect (twins) studies
- Fracture studies

AGENDA

WORKSHOP ON NEW DIRECTIONS IN METALLURGY

Wednesday, July 18, 1984

Introduction and Charge
Ben A. Wilcox, Assistant Director, MSD

Participant Presentation
Moderator: Phil Parrish, ARD

Brainstorming Session
Moderator: John Hirth, MRC

Workshop Breakouts
Moderated by MRC participants
(2 - 3 topics to be discussed)

Reports of workshop leaders

Workshop Summary Report
Williams, Mehrabian, Hirth